AN EVALUATION OF FORMIC ACID AS AN ELECTRON DONOR FOR PALLADIUM (PD) CATALYZED DESTRUCTION OF NITROAROMATIC COMPOUNDS

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Abstract

The Department of Defense is responsible for over 2,000 hazardous waste sites containing nitroaromatic compounds (NACs) such as 2,4,6-TNT, 2,4- and 2,6-DNT that resulted from the production and use of munitions throughout the nation and world. NACs are typically persistent in natural environments, though they can be oxidized or reduced under engineered conditions. NACs and their reduction products are toxic chemicals and suspected human carcinogens. Both TNT and 2,4-DNT are listed as priority pollutants by the U.S. EPA.

This study investigates the effectiveness of using a palladium (Pd) catalyst in concert with formic acid as an electron donor to reduce NACs. If the reduction reaction is rapid and complete, without producing hazardous daughter products, the process may have application as an *in situ* treatment technology to remediate NAC-contaminated groundwater.

In this study, formic acid was added into NAC-contaminated water flowing through a laboratory column filled with Pd catalyst. Experimental results using 2,4-DNT as a model NAC indicate reduction rates are dependent on pH, formic acid concentrations, and NAC concentrations. At high NAC concentrations and high pH, reduction rates slowed. Higher concentrations of formic acid led to greater extent and rates of 2,4-DNT reduction. The amines that would be expected to be produced from 2,4-DNT reduction were identified in the column effluent, along with several unidentified byproducts. Further research is required to identify and characterize the possible risks these unknown byproducts might pose. Based on experimentally observed reaction rates

and removal efficiencies, there is potential that Pd-catalyzed reduction using formic acid as a reductant may have application as an *in situ* remediation technology to manage NAC-contaminated groundwater.

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AN EVALUATION OF FORMIC ACID AS AN ELECTRON DONOR FOR PALLADIUM (PD) CATALYZED DESTRUCTION OF NITROAROMATIC COMPOUNDS

1.0 INTRODUCTION

1.1 Motivation

The Department of Defense (DoD) is home to over 29,000 hazardous waste sites. These sites are located on approximately 11,000 military installations and former properties in all 50 states, the District of Columbia, and the eight U.S. territories (DoD, 2003). Though clean-up activities are underway or complete at many of the sites, a significant number of sites still remain to be investigated and perhaps remediated. Administration of DoD sites falls under the Defense Environmental Restoration Program (DERP); a federally mandated program to remediate environmental contamination from past defense activities. A number of DoD sites listed in the DERP, currently 2,307, are contaminated with constituents of munitions such as 2,4,6-trinitrotoluene (TNT), 2,4- and 2,6-dinitrotoluene (DNTs) and nitrotoluenes (NTs), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrasocine (HMX) (DoD, 2003). These sites are broken down into three categories: active installation sites (542 sites identified), formerly used defense sites (FUDS) (1,691 sites), and Base Realignment and Closure Act (BRAC) sites (74 sites). The DoD has a significant stake in NAC remediation, only 15 out of the 542 active installation sites identified have investigations currently underway.

In the past 18 years, the DoD has spent almost $25 billion remediating hazardous waste sites through the DERP. The estimated cost to complete restoration at the reported active installation and FUDS sites (2,233 sites) totals $11.2 billion (DoD, 2003). In FY 2002 alone, approximately $1.9 billion was appropriated for environmental restoration activities. The DERP does not include operational ranges that are currently in use by the Department of Defense. There is little doubt that ranges currently in use will have munitions contamination that must be addressed in the future. The nitroaromatic compounds (NACs) and their byproducts found at these operational ranges present a potential hazard due to their explosive safety risks and potential toxicological effects (DoD, 2003). The DoD estimates that total remediation costs at operational ranges will be between $16 billion and $165 billion (DoD, 2003). These NACs are of interest as the nitro group is among the most common groundwater and soil contaminants in the U.S., second only to the organochlorine functional group (Agrawal and Tratnyek, 1996).

Trinitrotoluene is a xenobiotic oxidizing agent suspected of causing methemoglobinemia (Klaassen, 2001); in the bloodstream, it binds hemoglobin so oxygen transport through the body is limited. The DNTs are smooth muscle toxins that cause atherosclerosis, a cardiovascular disease that results in buildup inside arteries and reduces blood flow (Klaassen, 2001). Chronic toxicity studies in laboratory animals have shown DNTs can cause cancer of the liver, gallbladder, and kidneys as well as benign tumors of the connective tissue. It is also possible for munition constituents to be biologically transformed into toxins that are hepatotumorigenic; that is, which cause tumors in the liver. The toxicity and widespread use and occurrence of these chemicals within DoD make them an environmental concern.

Current techniques used to restore NAC-contaminated groundwater include pump-and-treat, bioremediation, and natural attenuation. The conventional technique for treating munitions-contaminated groundwater is a pump-and-treat system (DoD, 2003). The contaminated groundwater is pumped to the surface, and the NACs are removed by sorption to activated carbon. The treated groundwater is then returned to the aquifer or discharged to surface waters. The major disadvantage of this remediation strategy is that the contaminant is simply transferred from the liquid to the solid phase; the NAC itself is still present aboveground, on the activated carbon, and potentially harmful. The use of granular activated carbon (GAC) is the most common method of treatment due to its simplicity, effectiveness, and, at least in past years, its relatively low price. However, the rising cost of disposing or regenerating spent GAC is making other technologies more competitive (Rodgers and Bunce, 2001). In addition, activated carbon is not useful to treat high contaminant concentrations, as its sorption capacity may become rapidly depleted as contaminant mass loadings increase, thus, requiring frequent disposal or regeneration (Rodgers and Bunce, 2001). The increasing regulatory requirements and disposal costs associated with *ex situ* (that is, above ground) remediation technologies such as GAC have led researchers to look for more effective methods of treating contaminant in place, or *in situ*. Within the DoD alone, approximately $20 million are budgeted yearly for research and development of more effective remediation technologies (DoD, 2003).

In general, *in situ* treatment is safer, has less regulatory requirements, is more acceptable to the public, and usually is cheaper than *ex situ* treatment. The contaminant is remediated in the subsurface, so contact with the contaminant by site workers or the

general public is limited compared to when the contaminant is pumped to the surface as part of a pump-and-treat system. In many jurisdictions, the water that has been treated by a pump-and-treat system cannot be reinjected into the subsurface, and must be managed aboveground. Not only does aboveground wastewater management involve costs, it also may constitute a significant waste of a limited resource. In addition to eliminating aboveground waste management costs, the costs of pumping water to the surface are eliminated when treatment is *in situ*. For the above reasons, particularly the reduction in risk and the fact that all treatment is below ground, *in situ* treatment technologies are often viewed favorably by the public.

One *in situ* remediation technique being investigated for application to NAC-contaminated groundwater is engineered *in situ* bioremediation. Recent studies have shown NACs may be completely degraded to carbon dioxide and water in laboratory scale systems (Nishino *et al*., 1999). Engineered *in situ* bioremediation has all the advantages of *in situ* technologies that were discussed above, while also having the added advantage of using biological processes to destroy the NAC. Bioremediation of NACs has good potential as a future remediation strategy, though at present, field scale implementations are limited. While laboratory and bench scale NAC bioremediation studies have been successful, exhibiting high rates of degradation and complete mineralization (Nishino *et al*., 1999), these laboratory successes may not translate to field-scale application. Bioremediation is limited in its application and current studies suggest that high levels of DNT contamination (> 20 ppm) may inhibit microbial growth (Nishino *et al*., 1999). Bench scale studies have also shown other possible limitations to bioremediation: bioclogging due to excessive microbial growth, poor system

performance when oxygen levels drop (Lendenmann *et al*., 1998), and the difficulty of proper subsurface mixing of the target contaminant, electron donor, and microorganisms.

Natural attenuation, the degradation or removal of a contaminant by naturally occurring processes such as radioactive decay, chemical and biological transformation, or uptake by plants, is another possible method of remediation. Concentrations of NACs may also be reduced through sorption to soil or humic acids, dispersion, or volatilization. These processes occur naturally and do not require human intervention, unlike engineered bioremediation. Studies of NAC-contaminated natural systems have found that NACs are degraded extremely slowly with the production of toxic intermediate amino compounds (Nishino *et al*., 1999). Though microorganisms capable of mineralizing NACs exist in natural systems, they do not appear to degrade NACs at the rates seen in laboratory studies (Nishino *et al*., 1999).

Another method of remediation is chemically catalyzed degradation of NACs using a noble metal catalyst formulation. Pure metal catalysts like palladium are too costly for waste treatment and in certain instances the pure catalyst dissolves in the presence of NACs (Rodgers and Bunce, 2001). Metal catalyst formulations of Pd with carbon, iron, or Al_2O_3 have been used to degrade other environmental contaminants such as TCE and PCE (Lowry and Reinhard, 2001) and research has shown the process has potential for degrading NACs as well (Rodgers and Bunce, 2001; Phillips, 2003). Recent work using palladium as a noble metal catalyst to reductively degrade nitrotoluene showed that the reaction was sufficiently fast to be used in the field to remediate NAC-contaminated groundwater (Phillips, 2003). Palladium was used rather than other metal catalysts such as nickel, ruthenium, and platinum because palladium has been shown to

result in faster reaction kinetics (Niekamp, 2001). Swift reaction kinetics are necessary due to the limited residence time associated with *in situ* remediation techniques. The fast reaction kinetics that result from using just a small amount of palladium makes palladium an ideal catalyst for in-well treatment systems.

The noble metal formulation catalyzes reduction chemistry by providing a site for an electron donor and the contaminant to come together. There are a host of electron donors that could be used but most often H_2 gas and common acids such as hydrochloric, sulfuric, or formic acid are used. Until recently H_2 was the most commonly used electron donor but new studies have shown that using formic acid as an electron donor may result in faster contaminant reduction (Phillips, 2003). Studies conducted by Phillips (2003) showed formic acid produced NAC degradation rates superior to hydrogen. Formic acid offers several other advantages as compared to hydrogen. The major one is a buffering effect: the hydroxide ions formed during nitrate reduction are neutralized *in situ* at the catalyst surface by the CO_2 formed by the decomposition of formic acid (Prüsse and Vorlop, 2001). This buffering effect prevents the pH in the system from continuously rising as hydroxide ions are formed when the nitrite is reduced. When only hydrogen is used as an electron donor, the hydroxide ions raise the pH within the system. As the pH rises, catalyst deactivation occurs as a result of OH^- ions binding to catalyst sites (Phillips, 2003). Another advantage of using formic acid is its general safety. Liquid formic acid is easier to handle than compressed H_2 gas which is explosive and highly flammable. Formic acid also has a much higher solubility than H_2 and it is possible to make solutions with high concentrations of formic acid. The low solubility of molecular

hydrogen can limit the system as insufficient electron donor may be present at high NAC concentrations.

Though the kinetics of palladium-catalyzed degradation of NACs have been explored (Phillips, 2003), the reaction byproducts of NAC reduction using a Pd/Al_2O_3 catalyst with formic acid as an electron donor have not been identified. Reaction byproducts using other palladium formulations or other electron donors have been studied, however. Hydrogenation of 2,4-DNT using H_2 gas as an electron donor and a Pd on carbon catalyst was accomplished by Neri *et al*. (1995) with the main reaction intermediate being 4-hydroxylamine, 2-nitrotoluene (4HA2NT). Other intermediates found were 4-amino, 2-nitrotoluene (4A2NT) and 2-amino, 4-nitrotoluene (2A4NT) (Neri *et al*., 1995). These intermediates are not production chemicals and have little industrial use. Toxicity studies for these chemicals are limited, however amine-substituted chemicals are generally toxic (Williams and Burson, 1985). Amines are strong irritants and are easily absorbed by all routes. The nitro group and the amine group both cause methemoglobin formation in red blood cells reducing oxygen transport in the body. The reduction of 2,4-DNT using a Pd/Al_2O_3 catalyst with H_2 as an electron donor was studied by Rajashekharam *et al*. (1998). In their work, they found a reaction scheme as seen in Figure 1.1 almost identical to the one proposed by Neri *et al*. (1995).

The degradation products and pathways associated with the destruction of NACs are important for determining treatment methods and potential risks at a contaminated site. Both 2,4-dinitrotoluene and 2,6-dinitrotoluene, precursor chemicals and degradation byproducts of trinitrotoluene, have been shown to be carcinogenic in animals (EPA, 2002). In order to determine the feasibility of Pd-catalyzed degradation of NACs, the

byproducts and degradation pathways must be determined. The viability of Pd-catalyzed destruction of NACs as a remediation technology at DoD sites may hinge on whether or not significant quantities of daughter products that are more harmful than the parent NAC (such as the amines observed in Neri *et al.*'s (1995) work) are produced.

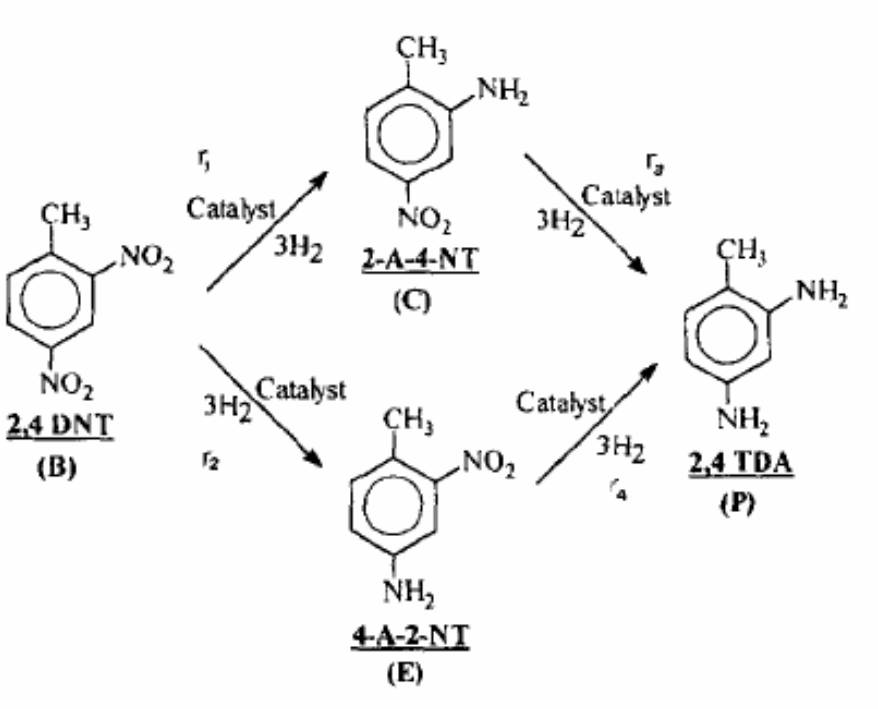

Figure 1.1 Reaction scheme for hydrogenation of 2,4-DNT (Rajashekharam *et al.*, 1997)

1.2 Research Objectives

This research will attempt to identify the reaction pathway and byproducts that result from the Pd-catalyzed reduction of NACs using a Pd/Al_2O_3 catalyst and formic acid as an electron donor. This thesis will focus on answering the following questions:

1. What byproducts result from the Pd-catalyzed degradation of a model NAC (nitrotoluene) using formic acid as an electron donor?

2. What are the reaction kinetics and rate parameters that describe the Pd-catalyzed degradation of nitrotoluene?

3. What byproducts result from the Pd-catalyzed degradation of a second model NAC (DNT) and its isomers? What are the key degradation pathways of DNT?

4. What byproducts result from the Pd-catalyzed degradation of more complex NACs (TNT, HMX, etc.)? What are the key degradation pathways?

1.3 Study Limitations

There are laboratory safety issues associated with the use of NACs like TNT, HMX, and RDX. As these chemicals are explosive and very dangerous even in small quantities they may not be used in the available facilities. This study will use nitrotoluene (NT) and 2,4-dinitrotoluene (2,4-DNT) as model NACs. These compounds are precursors to TNT and are expected to behave in a similar fashion though they possess fewer nitro functional groups, making them safer for laboratory use. Results from the 2,4-DNT experiments will be compared to results obtained by Rajashekharam *et al*. (1999). Degradation pathways for HMX and RDX will not be explored as no standards or precursor chemicals are available, or permitted in the available laboratory. This study will focus solely on NAC-contaminated groundwater and will not address NAC-contaminated soil or pure phase NAC.

2.0 LITERATURE REVIEW

2.1 Uses of Nitroaromatic Compounds (NACs)

NACs have been found to be ubiquitous pollutants in the aquatic environment because they are widely used as pesticides, explosives, chemical intermediates, and dyes (Heijman *et al*., 1995). Catalytic hydrogenation of nitroaromatic compounds is a process used for the production of aromatic amines that are used to make plastics, fine chemicals, and pharmaceuticals. One specific group of NACs is the (poly)nitrotoluenes consisting of a base toluene molecule with several nitro (NO_2^-) groups. Nitrotoluenes are high production chemicals with over 30 million pounds of *o*-nitrotoluene and over 10 million pounds of *p*-nitrotoluene produced in the U.S. each year (see Appendix D for chemical structures) (Dunnick *et al*., 2003). Hansen *et al*. (2001) reports that as of 1985, 2 million pounds of TNT were being produced per year. Hydrogenation of 2,4-dinitrotoluene (2,4-DNT) produces 2,4-diaminotoluene (2,4-DAT) which is used in the production of polyurethane (Neri *et al*., 1995). Dinitrotoluenes (DNTs) are intermediates in the manufacture of trinitrotoluene (TNT), once the world's most widely used explosive.

Explosives are one of the most significant uses of NACs. Thus, munitions manufacturing is a primary source of NAC contamination (Hansen *et al*., 2001). In military applications DNTs are primarily used as plasticizers and burn rate modifiers in propellants for rockets and artillery (Doppalapudi *et al*., 2001). DNTs are also precursors of toluene diisocyanate used to manufacture polyurethane foams (Nishino *et al*., 1999). DNT may also be found at industrial sites as it is a precursor to coatings and elastomers.

2.2 Production of Trinitrotoluene (TNT)

The chemical explosive, TNT, was first developed about 150 years ago. Though the explosive nitroglycerin was developed in 1846, TNT was not produced until 1863. TNT manufacturing began in the 1890's but production lagged until noted chemist Fritz Haber developed a process to synthesize ammonia in 1913. Readily available nitrogen increased manufacturing and TNT saw heavy use during WWI. Adapted to commercial use in the 1930's by Karl Bosch, the Haber-Bosch process lead to the mass production of TNT and other nitro compounds; in particular, fertilizers (Encarta, 2003). In the explosive production industry, TNT refers specifically to 2,4,6-trinitrotoluene, the most common and most used isomer of trinitrotoluene manufactured.

Production of TNT increased greatly in the first half of the 20th century. From WWI and WWII TNT production in Germany alone grew from 3,000 tons to over 20,000 tons per month (Urbanski, 1964). In the United States billions of pounds of TNT were produced annually. At the Weldon Spring Ordnance Works in eastern Missouri, more than 700 million pounds of TNT were produced from 1941 to 1945 (DoI, 1996), and Weldon Spring was only one of 23 Army Ammunition Plants in 21 states that were producing and storing TNT.

As a military weapon, TNT was ideal for delivering explosive destructive force, and destroying equipment, facilities, and materials. Since the turn of the century, TNT has been the major explosive used for ammunition throughout the world (Nahen *et al*., 1997). Only in the last 20 years has there been a shift to using other, more complex explosives, like HMX and RDX, in the military. TNT is still used in commercial

industry, and millions of pounds of TNT-based ordnance still may be found in the military inventory. During the middle of the 20th century, environmental regulations and constraints on treating and disposing of industrial wastes were almost non-existent. The production of TNT during this time resulted in large quantities of industrial effluent called "red water". Until about 30 years ago, hazardous substances and wastes, like "red water", were often managed and disposed of using standard practices that were later found to be detrimental to the environment (DoD, 2003).

2.3 Groundwater Contamination by NACs

A significant percentage of Department of Defense (DoD) contaminated sites that have been identified to date contain NAC contamination (DoD, 2003). These DoD sites can be found throughout the United States and at U.S. military bases in other countries. A majority of the contamination is the result of past and current manufacturing, storage, transportation, and detonation of explosives containing TNT. In looking at the history of TNT production and use it is easy to see how contamination infiltrated groundwater aquifers and surface waters. Urbanski (1985) reported that industrial "red water" contained up to 30 NACs besides TNT (Rodgers and Bunce, 2001). The "red water" contained residual amounts of TNT as well as other production chemicals; dinitrotoluenes (DNTs) and nitrotoluenes (NTs) being the most common. The NTs and DNTs are the raw materials used to make TNT. Nitration is carried out in the presence of nitric and sulfuric acid. A nitro group is added to toluene to form an NT which is further nitrogenated to DNT and finally to TNT. The TNT is then crystallized in alcohol or

water and then washed with sodium sulfite (Zhao and Yinon, 2002). The process water and wash water were then dumped directly to streams and wells often with no treatment of the effluent. Kratz (1949) reported that in Germany, for production of 4,000 tons of TNT a month, 5,000 – 6,000 m^3 of "red water" was generated daily (Urbanski, 1964). Though only 1.1 – 1.6% of drinking water samples test positive for DNTs with a mean concentration < 10 μg/L for all samples, waste streams from manufacturing plants have reported concentrations as high as 48 mg/L (CDC, 1998).

Another form of industrial waste from TNT production is "pink water" which was used for final cleaning and purification of the TNT. Pink water generated during loading, packing or assembling munitions often contains high concentrations of nitroaromatic explosives (Rodgers and Bunce, 2001). Wastewater contaminated with these explosives is also generated during demilitarization operations when excess or outdated munitions are destroyed (Adrian *et al*., 2003). Commonly today, the term "pink water" is used to describe all types of effluent containing nitroaromatic compounds due to the distinct pink color caused when TNT is photodegraded (Dave *et al*., 2000). Hwang *et al*. (1998) reported that a survey of four Army installations, where loading, packing, and assembling operations were carried out, found that 1.6 million gallons of "pink water" were produced annually.

Production and use of nitroaromatic explosives for military operations have resulted in their transfer into the environment where they pose an ecological and potential health hazard. Though the U.S. ceased commercial production of TNT in the mid 1980's, contamination still exists due to historical activities and current demilitarization operations (Rodgers and Bunce, 2001; Hwang *et al*., 1998). Production of TNT is now

limited to United States Army arsenals and data on production is not publicly available (CDC, 1995). U.S. Army arsenals are scattered across the United States, resulting in widespread TNT contamination in many states. Many of the former Army Ammunition Plants are now closed and listed on the National Priorities List (NPL), where the NPL is a listing of the most contaminated sites in the United States. These sites are identified in conjunction with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and billions of dollars have been spent to characterize and remediate them. The number and distribution of NPL sites that are contaminated by TNT (see Figure 2.1) indicates the widespread nature of this contaminant (CDC, 1995).

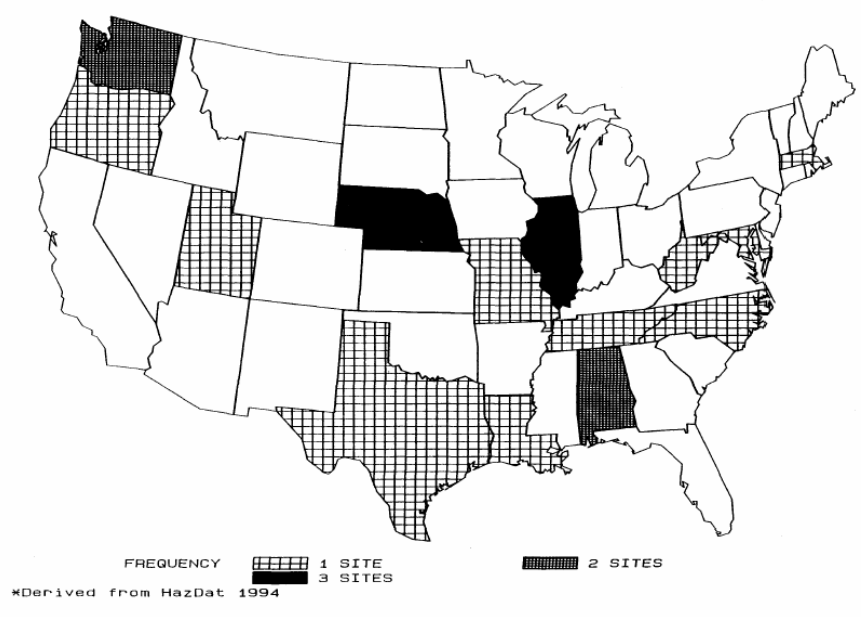

Figure 2.1 Location of NPL sites with TNT contamination (CDC, 1995)

Including degradation and products of combustion, there are over 200 chemicals associated with military munitions. Of the 20 of greatest concern, nine are directly associated with TNT, including TNT itself, and TNT degradation products like the

DNTs, nitrotoluenes, and amino-toluene isomers. DoD has identified potential releases of munitions at locations such as former ranges, open burning/open detonation sites and burial pits (DoD, 2003). The dinitrotoluenes are the major impurities of TNT and are usually present wherever soils have been contaminated with TNT. DNTs are also a major component of propellants for artillery shells, and can be found as contaminants in soils on firing ranges in the immediate vicinity of firing points (Pennington, 2003). The DNTs are more widely distributed across the United States than TNT (CDC, 1998) as can be seen by comparing Figure 2.1 with Figures 2.2 and 2.3. Crockett *et al*. (1995) listed some activities that result in soil or groundwater contamination by NACs, including open detonation and burning of explosives at army depots, evaluation facilities, artillery ranges, and ordnance disposal sites (Rodgers and Bunce, 2001). These activities continue today as military forces conduct training and improve military equipment and tactics.

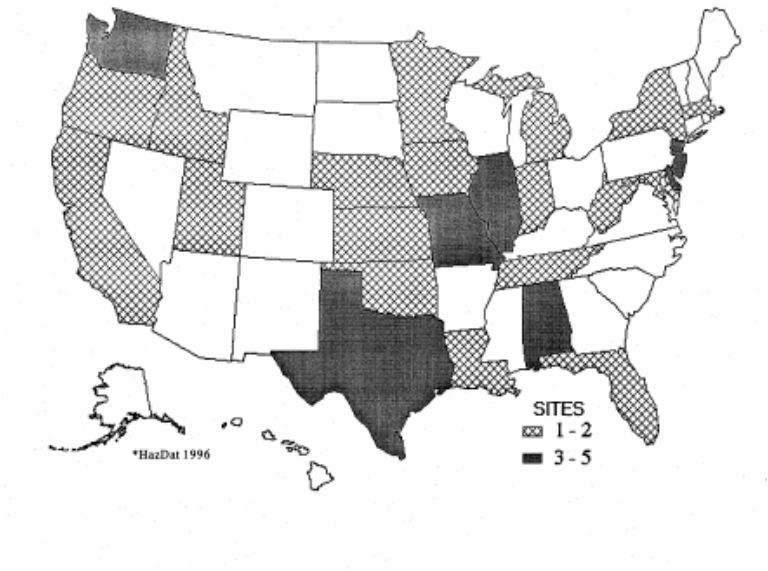

Figure 2.2 Location of NPL sites with 2,6-DNT contamination (CDC, 1998)

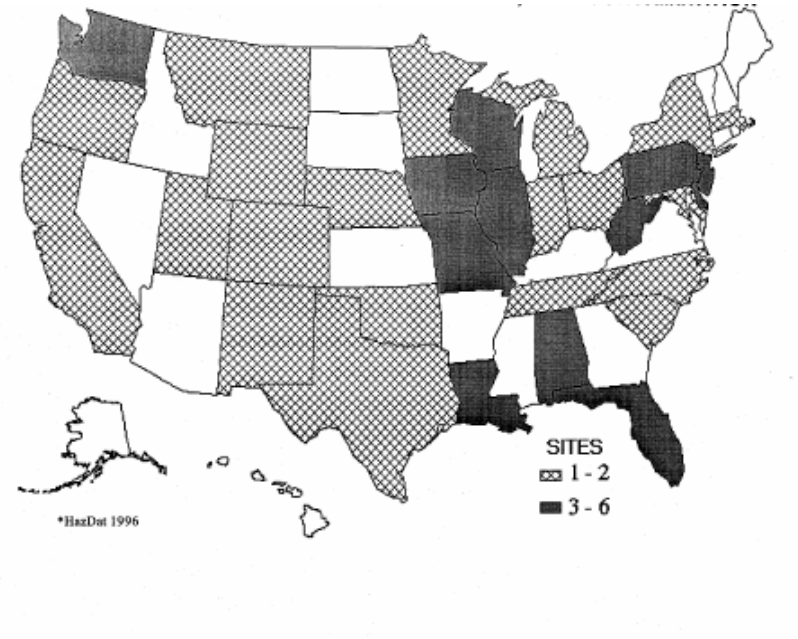

Figure 2.3 Location of NPL sites with 2,4-DNT contamination (CDC, 1998)

Military operations are vital in today's world. To attain the level of readiness necessary to deter adversaries and defend our nation, the DoD must develop, test, and deploy weapon systems and military munitions, and then train its personnel to use and maintain these systems (DoD, 2002). The past, present, and, presumably, future use of explosives will continue to cause nitroaromatic contamination. In 1993 the DoD had identified more than 1,000 sites with explosives contamination. Of these sites, greater than 95% had TNT and 87% exceeded permissible groundwater contaminant levels (Rodgers and Bunce, 2001). Adrian *et al*. (2003) report that more than 1,200 explosive contaminated sites have been identified within the United States. The extent of the problem is just beginning to be realized in Europe where more than 2,000 ammunition production and storage sites are likely contaminated with explosives. Lendenmann *et al*. (1998) report that traces of DNT have been found in the Rhine and Elbe rivers, two major

European waterways. Dillert *et al*. (1995) report that in Germany several places are known where the water supply is endangered by nitroaromatic compounds. Recent surveys of five Canadian anti-tank ranges revealed low level soil contamination by TNT, HMX, and RDX (Groom *et al*., 2001). The manufacture and use of these chemicals will continue in an effort to protect the security of our nation. However, their use has resulted in severe contamination of both soils and groundwater (Balakrishnan *et al*., 2003). With the inevitability of these chemicals being used in the future, along with widespread existing contamination, methods must be developed to remediate them and reduce the risk they pose to the public and the environment.

2.4 Toxicity of Nitrotoluenes, Aminonitrotoluenes, and Aminotoluenes

Many munition constituents are toxic and believed to be carcinogenic. TNT as well as 2,4-DNT are listed as U.S. EPA priority pollutants; they are known mutagens and can cause pancytopenia as a result of bone marrow failure (Rodgers and Bunce, 2001). This has focused the majority of toxicity research on TNTs and DNTs; the aminotoluenes have not been as studied and limited information is available. Trinitrotoluene is an oxidizing xenobiotic agent suspected of causing methemoglobinemia (Klaassen, 2001). The TNT causes a buildup of methemoglobin which leads to reduced oxygen levels by binding up hemoglobin making it unable to transport oxygen in the body. The precise mechanism is still unknown, but it is believed the nitro group in the TNT molecule directly interacts with the iron in hemoglobin reducing red-blood cell activity. Water phase toxicity studies conducted by Dave *et al*. (2000) resulted in a water-phase EC/LC_{50}

between 5 and 20 mg/L for two crustaceans (*Daphnia magna* and *Nitocra spinipes*). The toxicity of DNT to these crustaceans was slightly less than that of TNT, but after activation by UV light, DNT toxicity was more pronounced (Dave *et al*., 2000).

The DNTs are responsible for a number of occupational diseases including the cardiovascular disease atherosclerosis. In this case the toxic DNT degrades the interior of arteries causing plaque buildup and obstructing bloodflow. DNT appears to have a negative effect on Sertoli cells causing sterility (Klaassen, 2001). DNTs have also been identified as smooth muscle cell toxins (Klaassen, 2001). The toxin mutates the cell and can cause uncontrolled growth similar to a tumor. Chronic toxicity studies in laboratory animals have shown that DNT can cause cancer of the liver, gall bladder, and kidney, as well as cause benign tumors of the connective tissue. In humans, retrospective mortality studies in exposed workers show DNT causes circulatory disorders of atherosclerotic etiology. DNT can also be biologically transformed to more toxic contaminants that are hepatotumorigenic; that is, which cause tumors in the liver (Klaassen, 2001). During WWI and WWII, fatal cases of toxic jaundice and aplastic anemia were recorded by the U.S. Department of Health and Human Services among munitions workers (Rodgers and Bunce, 2001). Urbanski (1964) reported that in one ammunition plant in the U.S., 17,000 poisoning cases with 475 fatalities occurred during seven and a half months of production.

Since DNTs are considered toxic and many explosives-contaminated sites exhibit DNTs as well as TNT, the fate of DNT is relevant to remediation and risk assessment (Pennington, 2003). Hawari (1999) reports that the environmental transformation products of NACs, including arylamines, arylhydroxylamines, and condensed products

such as azoxy- and azo-compounds, are thought to be as or more toxic than the parent nitroaromatic (Rodgers and Bunce, 2001).

The aminonitrotoluenes (2A4NT and 4A2NT) which were seen as intermediates in the reduction of DNT (Neri *et al.,* 1995; Rajashekharam *et al*., 1998) have not been studied with the same intensity as TNT and the DNTs. Specific toxicological studies using these chemicals could not be found, but the chemical properties of the functional groups may be used to infer toxicity. Chemicals with the amine (NH_2) functional group are usually strong irritants, have tissue-corrosive characteristics, and can cause methemoglobin formation (Williams and Burson, 1985). The nitro group (NO_2) is believed to be responsible for causing methemoglobinemia as seen with TNT and the DNTs and its presence indicates the aminonitrotoluenes may have similar effects.

The diaminotoluenes (DATs) are significantly more common and toxicity studies have shown DATs cause hepatocellular carcinomas (the most common primary malignant liver tumor) in rats and mice (Hathaway *et al*., 1996; Klaassen, 2001). Exposure to 2,4- and 2,6-diaminotoluene also inhibited DNA synthesis in smooth muscle cells, similar to the effects caused by 2,4-DNT (Klaassen, 2001).

The nitrotoluenes (2-NT, 3-NT, 4-NT) have been shown to depress the immune system and antibody response, thus lowering host resistance. 2-NT exhibited clear evidence of causing cancer at multiple sites in rats and mice. These studies showed that experimental exposure to 2-NT caused mesotheliomas, subcutaneous skin neoplasms, mammary gland fibroadenomas, and liver neoplasms. Stop-studies, experimental treatment with 2-NT for a set period of time, on rats and mice showed tumor formation occurred after three months of dosing at 125 mg/kg or 315 mg/kg and these events were

irreversible and eventually lead to cancer at multiple sites (Dunnick *et al*., 2003). The aminotoluenes, also called toluidines (see Appendix D), are demonstrated mutagens that have been shown to be carcinogenic in animals and are suspected human carcinogens (Williams and Burson, 1985). They also cause anoxia as a result of methemoglobin formation (Hathaway *et al*., 1996).

2.5 Properties of Nitroaromatic Compounds

The high yield detonation, ease of ignition, and relatively safe handling (compared with nitroglycerine) of TNT made it an ideal explosive that could be mass produced, stored and shipped (Lewin, 2003). The low melting point (80.1°C), stability, low sensitivity to impact, and safety of manufacture, compared to other explosives, were additional benefits of TNT (Doppalapudi *et al*., 2001). Nitroaromatic compounds are resistant to chemical or biological oxidation and to hydrolysis because of the electron-withdrawing nitro groups (Rodgers and Bunce, 2001). They are environmentally persistent and remediation of NAC-containing waste streams and groundwater is difficult due to their properties. TNT has a solubility of 130 mg/L at 20ºC (CDC, 1995) which causes soil contamination to slowly seep into the groundwater. The DNTs have only a slightly higher solubility of 270 mg/L at 20ºC. The octanol/water partition coefficient as log K_{ow} is 1.60 so TNT is not expected to significantly partition to sediment or strongly sorb to soil particles (ICSC, 2000). The average adsorption coefficient (K_d) for soil tests conducted by Pennington and Patrick (1990) was 3.8 cm^3/g with a standard deviation of 1.34 (Phelan and Webb, 1998) indicating limited sorption potential. TNT has a relatively

low Henry's Law constant, $3.35x10^{-7}$ indicating limited partitioning from surface waters to the atmosphere (Phelan and Webb, 1998).

Based on these parameter values, it appears that removal of aqueous phase TNT due to volatilization or sorption is limited. Thus, solid TNT at the surface, which has been reported to persist for many years by Rosenblatt (1980) will act as a source of groundwater contamination, dissolving into water with very little removal by either volatilization or sorption (CDC, 1995).

2.6 Reduction of NACs

Although, as noted earlier, oxidation of TNT and other NACs is difficult, these compounds are susceptible to chemical reduction. Engineered reduction of NACs has been proposed as the first step in a two-stage treatment process, since the aromatic polyamines that result from NAC reduction are more biodegradable, less persistent and/or bind irreversibly to the solid matrix under oxic conditions (Hofstetter *et al*., 1999) compared with the parent nitroaromatic. Hoffstetter *et al*. (1999) reports that reduction of nitro groups is the predominant transformation pathway of polynitroaromatics under anaerobic as well as aerobic conditions. During reduction, the nitro groups (NO_2) are replaced with amine groups (NH_2) in a sequential order. The TNT is reduced down to triaminotoluene (TAT). Under aerobic conditions, DNTs are reduced to monoaminodinitrotoluenes, but not to diaminonitrotoluenes (Pennington, 2003).

Reduction of NACs can be accomplished by creating a reducing environment by oxidizing a metal, such as Fe, or by using an electron donor, such as hydrogen or formic

acid, in the presence of a catalyst. Heijman *et al*. (1995) investigated the role of surface-bound iron species (Fe(III)), which served as a mediator for electrons originating from microbial oxidation of organic material by iron reducing bacteria, in the reduction of NACs. All of the nitroaromatic compounds investigated were reduced to the corresponding amino compounds. The nitro group attached to the aromatic ring was reduced by the addition of electrons. The oxygen molecules were removed and combined with free hydrogen to form water. Then two hydrogens and two electrons bind to the nitrogen forming the NHOH hydroxylamine group. The second oxygen is removed by the addition of the final two electrons and the oxygen combines with hydrogen to again form water. The process can be seen in Figure 2.4 below. It was found that regeneration of reactive sites was rate limiting, while electron transfer to the NAC was fast (Heijman *et al*., 1995). Under anoxic conditions, NACs may be reduced to the corresponding hydroxylamines and ultimately to the amines (Heijman *et al*., 1995).

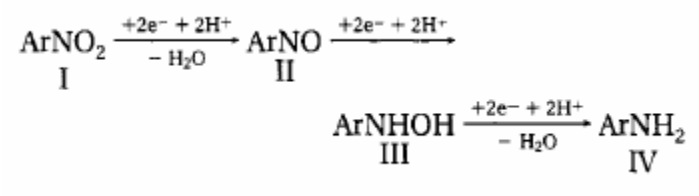

Figure 2.4 Aromatic(Ar) ring (I) reduced to corresponding hydroxylamine (III) and, ultimately to amine (IV) (Heijman *et al*., 1995)

Other NACs are reduced by similar mechanisms. Nitrobenzene is reduced in the presence of zero valent iron under anaerobic conditions to aniline with nitrosobenzene as an intermediate (Agrawal and Tratnyek, 1996). Other studies of NAC contaminant remediation with zero-valent metals have been reported and these studies support the view that contaminant degradation results from reduction coupled to metal corrosion

(Agrawal and Tratnyek, 1996). The transformation reaction generally produces the corresponding aromatic amines, with minor amounts of intermediates like hydroxylamines and nitroso compounds (Agrawal and Tratnyek, 1996).

Granular iron has been determined to be a potentially useful reductant for organic contaminants in groundwater. Devlin *et al*. (1998) used a suite of NACs to investigate granular iron reactivity. The research found the NACs were rapidly reduced to anilines that sorbed to the solid iron particles, thereby reducing the activity of the iron. The granular iron reactivity was rapidly reduced over the first few days then more slowly over several months (Devlin *et al*., 1998). Nitro reduction by iron may be useful in the treatment of NAC-contaminated water if the resulting amines can be removed by subsequent treatment (Agrawal and Tratnyek, 1996). Triaminotoluene (TAT) may be almost irreversibly bound to the granular iron surface. Treatment of TNT with iron may lead to very small residual dissolved concentrations of TNT and its reduction products over prolonged periods (Devlin *et al*., 1998). Research has demonstrated that NACs such as TNT can be completely reduced to the corresponding aromatic polyamines by Fe(II) present at the surface of Fe(III)(hydr)oxides (Hofstetter *et al*., 1999).

A second method of reduction involves using a metal catalyst and an electron donor. Many different metal catalysts exist; nickel rhodium, platinum and palladium being the most common. More recently palladium metal and metal formations made with palladium have been used as catalysts because of their superior performance over other metals (Niekamp, 2001). Hydrogenolysis of PCE on Pd has been demonstrated and shown to be faster than PCE reductive dechlorination in the presence of iron (Devlin *et al*., 1995). There are also many different electron donors that can be used to drive

reduction of NACs. The most commonly used electron donor is hydrogen gas, H_2, which creates the needed free electrons and hydrogen to reduce the contaminant. Another potential electron donor is formic acid. Recent studies by Phillips (2003) have shown that formic acid is a superior electron donor for the Pd-catalyzed reduction of NACs. There has been limited research conducted on Pd-catalyzed degradation of NACs. Hydrogenation of 2,4-DNT to 2,4-diaminotoluene (DAT), also called 2,4-toluenediamine (2,4-TDA), using H_2 gas as an electron donor was carried out over a 5% Pd/C catalyst (Neri *et al*., 1995). The main reaction intermediate was 4-hydroxylamine, 2-nitrotoluene (4HA2NT). The other two relevant intermediates that were observed were 4-amino, 2-nitroluene (4A2NT) and 2-amino, 4-nitrotoluene (2A4NT) (Neri *et al*., 1995). Researchers determined intermediates are formed from DNT through two parallel reactions (Figure 2.5). The intermediates are then hydrogenated to produce DAT, as shown in Figure 2.5 (Neri *et al*., 1995). The reaction pathway shows the sequential removal of oxygen and replacement by hydrogen. Similar behavior is seen when Pd/Al_2O_3 is used as a catalyst and hydrogen gas is the electron donor (Rajashekharam *et al*., 1997). The researchers reported two possible reduction pathways similar to those shown in Figure 2.6. The first pathway has 4HA2NT as an intermediate while the other pathway bypasses hydroxylamine production. Rajashekharam *et al*. (1997) reported that the 4HA2NT intermediate accounted for less than 2% of the 2,4-DNT that was converted and therefore could be discounted in the stoichiometric reaction pathway.

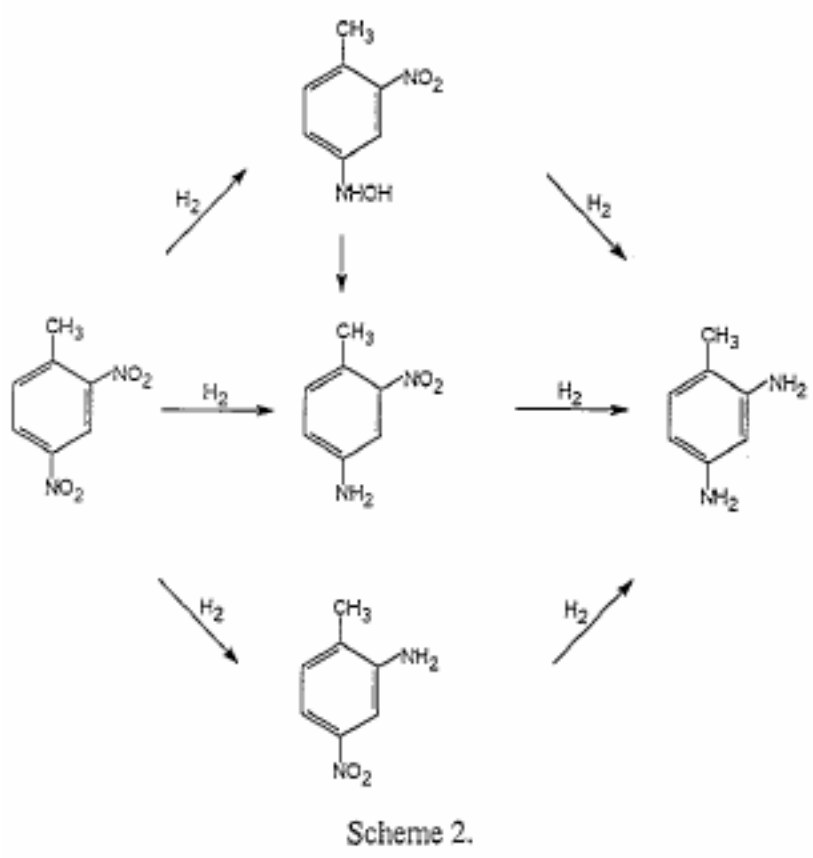

Figure 2.5 Reduction pathways for 2,4-DNT (Neri *et al.*, 1995)

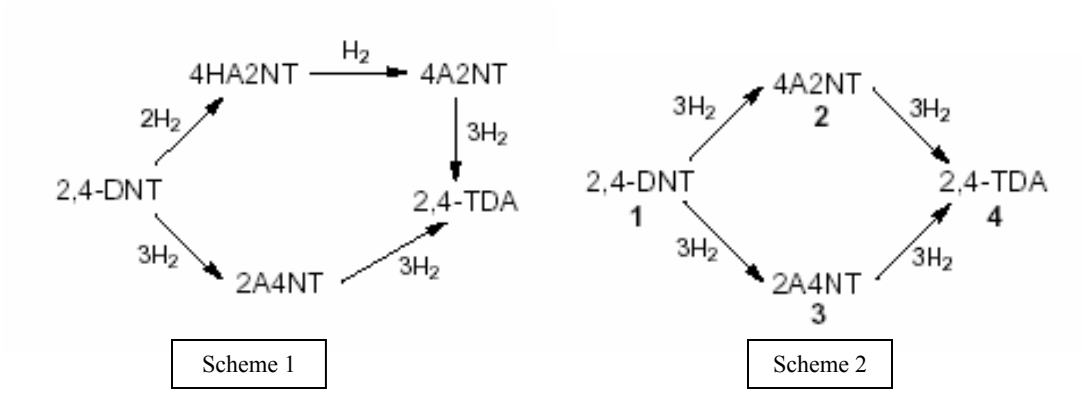

Figure 2.6 Two possible pathways for the reduction of 2,4-DNT (Rajashekharam *et al.*, 1997)

Reduction by palladium catalysis is ineffective at high pH, as strongly adsorbing oxygenated species block palladium sites (Prüsse and Vorlop, 2001). This inhibits the Pd reactivity. Studies conducted by Prüsse and Vorlop (2001) found that for Pd-catalyzed nitrite reduction with hydrogen gas as a reductant, the activity of the nitrite decreases with increasing pH (Prüsse and Vorlop, 2001). Research conducted by Phillips (2003) also showed that degradation rates decreased with increasing pH. One advantage that is hoped to be gained using formic acid is an internal buffering effect to control the pH.

Formic acid combines with palladium to produce a reducing environment through a mechanism that Prüsse and Vorlop (2001) describe as transfer hydrogenation. Transfer hydrogenation is the process by which formic acid binds to palladium at two congruent sites (Figure 2.7). One hydrogen is released as the formic acid binds, the other then is available for immediate use in the reduction of the NAC contaminant. This reduction occurs as described in Figure 2.5. When starting with DNT as a contaminant, byproducts like those reported by Neri *et al*. (1995) and Rajashekharam *et al*. (1997) are seen.

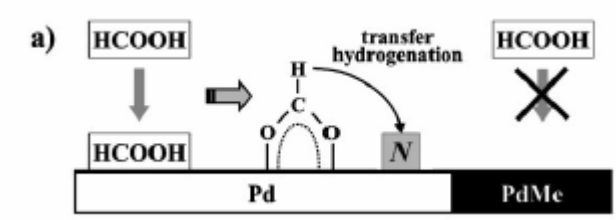

Figure 2.7 Schematic representation of the absorption of formic acid onto monometallic Pd (Prüsse and Vorlop, 2001)

To date, only Phillips (2003) is known to have looked at a system using a palladium catalyst and formic acid as an electron donor to remediate NACs. Both Neri *et al*. (1995) and Rajashekharam *et al*. (1997) used H_2 gas as a reductant. A number of advantageous properties of formic acid may account for its superior performance.

Formic acid is a liquid that has almost unlimited solubility in water so high concentrations of formic acid can be achieved; whereas hydrogen gas has a limited solubility. Formic acid also buffers the system due to the production of CO_2 as the acid breaks down during reactions with the palladium. The hydroxide ions formed during nitrate reduction are neutralized at the catalyst surface (Prüsse and Vorlop, 2001). Formic acid is also cheaper and easier to store, ship, and handle as compared to a compressed gas like hydrogen.

2.7 Application of Pd Catalyzed Reduction of NACs

Metal catalyst systems used for groundwater remediation may be applied either aboveground in conjunction with pump-and-treat systems or in-well as an *in situ* remediation technology. For *in situ* application, a catalyst can be installed in-well as a component of a recirculating well. In this type of well, contaminated groundwater is extracted from the aquifer through a well screen, pumped up through the well where it passes through the catalytic reactor, and the treated water is then injected into the aquifer through a second well screen. A fraction of the treated water then flows through the aquifer back to the extraction well screen for recycle through the in-well reactor. Another approach is to use so-called horizontal flow treatment wells that have two dual-screened wells that pump in opposite directions (one well pumps water up, the other down). Recycle occurs between the two wells, with treatment occurring as water passes through in-well reactors. The high rates of degradation that have been seen with Pd catalysis make Pd an ideal choice for in-well application where fast reaction kinetics are

required due to the limited contact time in the reactors. Formic acid may be useful as a reductant in an in-well system, based on the advantages of its use which were discussed above.

2.8 Alternate NAC Remediation Technologies

2.8.1 Ex Situ Technologies.

There are a number of technologies available to remediate NAC contamination in groundwater at the surface, or *ex situ*. A pump-and-treat system is used to capture contaminated groundwater and pump it to the surface. Methods of treatment that can be employed at the surface include physical processes such as adsorption to activated carbon, biological processes like bioremediation or phytoremediation, and chemical processes such as photocatalytic degradation. Physical adsorption using granular activated carbon (GAC) is a simple and commonly used method of remediation (Rogers and Bunce, 2001). The NACs are concentrated in the GAC and then the GAC is treated either through disposal, incineration, or regeneration by partial oxidation where the NACs desorb and burn (Rogers and Bunce, 2001). Pump-and-treat systems using adsorption to GAC as the aboveground treatment technology have been used in the field with much success. The use of GAC is limited due to the finite capacity of the activated carbon and the necessity to treat the GAC after use. At high contaminant concentrations and large groundwater volumes the use of activated carbon systems becomes economically unviable.

Bioremediation is another technology that can be linked to a pump-and-treat system. The contaminated groundwater can be pumped through fluidized beds or trickling filters where biologic activity can degrade the NACs, much like a municipal wastewater treatment systems. The use of bioremediation has the potential advantages of low cost, ease of operation and public acceptance (Rogers and Bunce, 2001). Another distinct advantage of bioremediation is that the NAC is destroyed rather than just removed as in GAC systems. Research has shown that bacteria can completely degrade mixtures of DNT liquid cultures without the production of aminonitrotoluenes (Nishino *et al*., 1999), though Nishino *et al*. (1999) found the presence of high concentrations (250 μM) of 2,6-DNT inhibited 2,4-DNT degradation. Biological systems also require a significant measure of control to ensure proper environments are maintained to support the microorganisms. Lendenmann *et al*. (1998) reported that loss of environmental control led to contaminant breakthrough in two instances.

E*x situ* chemical methods of remediation are also possible. One is photocatalytic degradation using ultraviolet light and an oxidizing agent such as hydrogen peroxide, ozone, or titanium oxide (TiO_2) to oxidize NACs (Nahen *et al*., 1997). The NACs absorb sunlight, or artificially generated UV light, and are oxidized (Nahen *et al*., 1997). Nahen *et al*. (1997) found that greater than 99% TNT removal was achieved within 90 minutes of irradiation. The major intermediates seen were trinitrobenzene, 3,5-dinitroaniline, 2A-4,6-DNT, and 4A-2,6-DNT (Nahen *et al*., 1997). In particular, the amino-dinitro compounds appear to accumulate during TNT photocatalysis (Nahen *et al*., 1997). Dillert *et al*. (1995) found that the reactivity of the NAC decreases with increasing numbers of nitro groups on the aromatic ring for irradiated aqueous suspensions of TiO_2.

Dillert *et al*., (1995) indicates that photocatalysis may be an effective treatment for ammunition plant wastewater, but does not report any successful field applications. Base-induced transformation of TNT has also been shown using NaOH (Hansen *et al*., 2001). Complete removal of TNT was reported with a systematic production of unidentified byproducts (Hansen *et al*., 2001).

2.8.2 In Situ Technologies.

In situ technologies have an advantage in that the contaminated groundwater remains in the subsurface. This greatly reduces the risk of exposure to the general public and reduces some of the regulatory requirements of dealing with hazardous waste. *In situ* remediation strategies are generally more economical for large scale clean-up as the cost of pumping millions of gallons of groundwater to the surface is not incurred. Though physical and photocatalytic methods of remediation are not practical to apply *in situ*, *in situ* biodegradation and chemical reduction are possible.

Spanggord *et al*. (1991) found that strains of *Pseudomonas* sp. under aerobic conditions could completely biodegrade 2,4-DNT, while using it as the sole source of carbon. A dioxygenase attack at the 4,5 position removed the nitro group as nitrite with subsequent reactions resulting in the removal of the second nitro group and complete biodegradation (Spanggord *et al*., 1991). Studies have found that TNT was transformed to 2,4,6-triaminotoluene (TAT) by *Clostridia* in Brain Heart Infusion broth, mixed cultures in anaerobic sludge, and by a biofilm from an industrial wastewater treatment plant (Adrian *et al*., 2003). Adrian *et al*. (2003) found that addition of H_2, ethanol, or propylene glycol enhanced transformation of TNT, which was completely depleted with

transient formation of 2A-4,6-DNT, 4A-2,6-DNT, 2,4DA-6-NT, and TAT. Findings indicate hydrogen is a key factor in stimulating the anaerobic biotransformation of RDX, HMX, and TNT and suggest the addition of hydrogen gas or electron donors that produce hydrogen gas may be a useful strategy for enhancing the anaerobic biodegradation of explosives in contaminated groundwater and soils (Adrian *et al*., 2003).

Though mineralization is possible, several factors can limit biodegradation. Bioavailability of some nitroaromatic compounds in historically contaminated soils can be dramatically reduced due to sorption to soil (Nishino *et al*., 1999). Bioremediation systems can be subject to mechanical failures as seen in experiments conducted by Lendenmann *et al*. (1998). Conclusions drawn by Schmelling (1996) and reported by Rogers and Bunce (2001) show that due to NAC toxicity, bioremediation may not be appropriate when NAC concentrations are high, or when biodegradation results in the production of non-biodegradable byproducts. Abiotic systems, like palladium catalyzed reduction systems, can be applied at areas with extremely high concentrations (>100 ppm) that are toxic to microorganisms. Research with Pd/formic acid systems is limited but encouraging requiring more research and efforts to identify daughter products and describe the system.

3.0 EXPERIMENTAL MATERIALS AND METHODS

3.1 Chemicals

Certified ACS grade chemicals were obtained from Sigma-Aldrich Chemical Co. in the highest purity available. No additional purification was performed and chemicals were used from their original containers as shipped. Chemicals obtained included all of the amino compounds used during the course of experimentation and two dinitrotoluene isomers; 2,4-dinitrotoluene and 2,6-dinitrotoluene. The isomers of the mononitrotoluenes (2-NT, 3-NT, and 4-NT) were obtained in 2002 by Lt Landon Phillips in his previous work (Phillips, 2003). These three chemicals have been in storage in their original containers in the Wright State University Department of Geological Sciences laboratory where the experiments were conducted. The nitrotoluenes were obtained from Sigma-Aldrich Chemical Co. and are certified ACS grade chemicals with a 99%+ purity.

3.2 Palladium Catalysts

Palladium catalysts were supplied by Sigma-Aldrich Chemical Co. as 0.5% weight on alumina (Al_2O_3) 3.2 mm diameter pellets. The pellets were used as obtained and no further purification was accomplished. The pellets were used as the sole media in the column reactor. The pellets were added to the column with no special precautions to avoid exposure to air.

3.3 Column

The column and end caps were purchased from Mainline Supply, Dayton, OH, a local plumbing supply store. The column is a 4 cm diameter, 316 gauge stainless steel tube. The column is 13 cm long and threaded on both ends. End caps of the same material were tightened with a wrench after Teflon tape was applied to the threads. A single, threaded hole of ¼" diameter was drilled into each end cap for installation of a sampling port. Each end cap was packed with a layer of pesticide grade glass wool obtained from Sigma-Aldrich Chemical Co. to ensure even flow across the column and prevent the media from infiltrating or clogging the tubing. The column was packed with 157.31 gm of Pd/Al_2O_3 pellets. The column was tapped repeatedly during packing to settle the pellets and reduce the pore volume. Once the end caps were applied and tightened, the column was not opened again, nor was it rotated from its original vertical orientation. The column remained vertical throughout the entire run of experiments with the influent entering from the bottom of the column and the effluent exiting the top of the column. Five pore volume measurements were made after the end caps were tightened, resulting in an average pore volume of 69.2 mL with a standard deviation of 2.28 mL. This pore volume was used to calculate hydraulic residence times (HRTs) during the subsequent experiments.

3.4 High Pressure Liquid Chromatograph (HPLC) - Standardization

Chemical constituents, daughter products, and concentrations were determined using a High Pressure Liquid Chromatograph (HPLC) detection system. The HPLC

system consists of a Dynamax® Solvent Delivery System, model SD-200. The delivery system uses two pumps, one pumping HPLC grade acetonitrile, the other pumping a buffer solution made with filtered deionized water and 10 mL of buffer solution concentrate (potassium phosphate monobasic-sodium hydroxide buffer, Fisher Scientific) per liter of water. The acetonitrile/buffer solution runs through a mixing chamber then through the sample injection ring. The sample injection ring has a volume of 20 μL. The detector is a Dynamax® absorbance detector model UV-1. The entire system is connected to a desktop computer and controlled by Dynamax® software. Output from the UV detector was obtained real-time and stored on the computer hard drive. Printouts of each sample run were collected as a backup. The column used was a Discovery® C-18 5μm, 25 cm x 4.6 mm HPLC column obtained from Supelco, a division of Sigma-Aldrich Chemical Co. The column was used with a 50% mix of HPLC grade acetonitrile (99.93%+, Sigma-Aldrich) and 50% buffer solution described above (pH > 6.5).

Calibration of the column was accomplished using multiple dilutions of known contaminant concentrations. Stock solutions of experimental chemicals were made from the above mentioned chemicals using filtered deionized water. Retention time ranges for each chemical were determined for the HPLC method used. Known concentrations were plotted against the absorbance area, resulting in a straight line relationship between concentration and area. Linear regression from the dilution standards gave R^2 values greater than 0.99 for all chemicals (see Appendix C).

All HPLC analysis was conducted at a flowrate of 1.3 mL/min and a UV absorbance of 254 nm. This wavelength is the maximum absorbance for the benzene ring and is appropriate for detection of most NACs. The nitrotoluenes mentioned above,

including the aminonitrotoluenes, are all clearly visible using the method parameters detailed above. The flowrate is the same as that used by Phillips (2003) though he used an absorbance wavelength of 280 nm. Other researchers including Lendenmann *et al*. (1998) and Heijman *et al*. (1995) used a wavelength of 254 nm in conjunction with HPLC for determination of NAC concentration. Heijman *et al*. (1995) also used HPLC with a flowrate set to 1.0 ml/min.

3.5 Flow-through Column Experiments

Flow through column experiments were conducted to identify daughter products formed by the reduction of nitroaromatic compounds on Pd catalyst using formic acid as an electron donor. Deionized water contaminated with a known concentration of a specific contaminant was pumped through the column using a Masterflex® L/S Digital Standard Drive peristaltic pump model number 7523-70 obtained from Cole-Parmer. The pump head is a PTFE diaphragm pump model number 07090-42 manufactured by the Barnant Company, Barrington, IL, and was obtained from Cole-Parmer.

Water used in the column experiments was mixed in a 19L glass jar where formic acid concentrations and pH could be adjusted to desired levels (see Figure 3.1). To adjust the pH, NaOH (1M and 2M) was added until the desired pH was obtained. Then 4 L of the mixture was placed in a glass Ehrlenmeyer flask and the contaminant was added to obtain the desired concentration (see Figure 3.1). Contaminant concentrations ranged from 20 ppm to 100 ppm. The contaminant-spiked mixture was then stirred for approximately 48 hours (72+ hours for the 100 ppm experiments) to ensure contaminant

was totally dissolved. Catalyst column influent contaminant concentrations were reduced over time as water with formic acid from the 19 L jar flowed into and diluted the contaminant-spiked water in the Ehrlenmeyer flask (Figure 3.1).

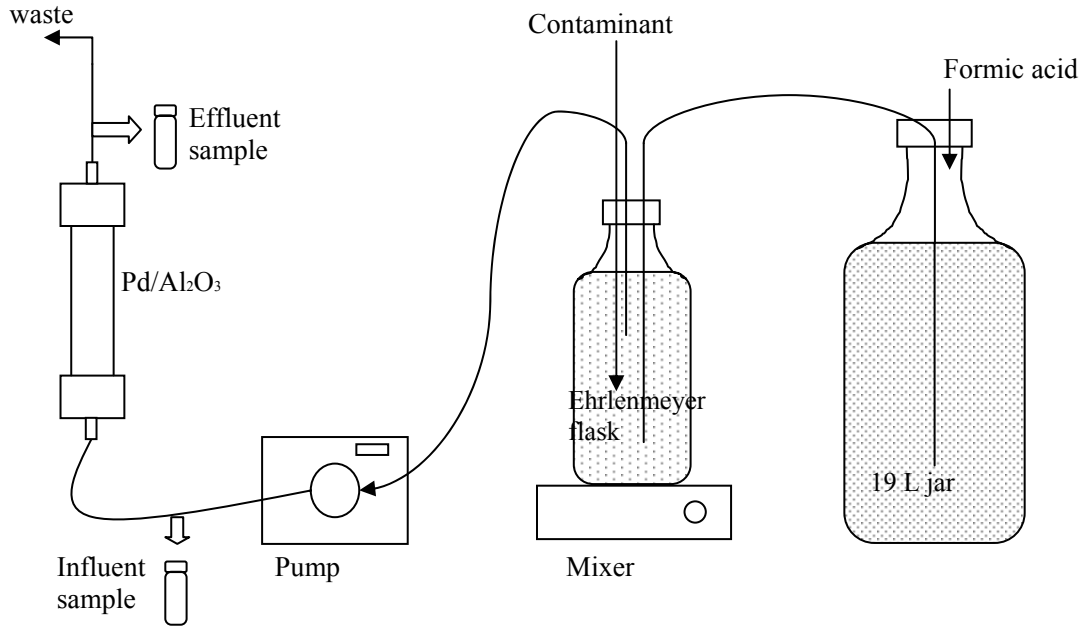

Figure 3.1 Schematic of experimental setup

Influent samples, C_{in}, were taken using a three-way valve (Cole-Parmer) after the flow passed through the pumphead prior to entering the column. The effluent samples, C_{out}, were taken from the column effluent line directly. Effluent samples were taken one minute after the corresponding influent sample. Flowrates through the column were determined for each experiment by running non-contaminated water from the 19 L jar through the column. The water was run until the measured effluent pH and conductivity stabilized. Pump settings were chosen to provide hydraulic residence times as close to one minute as possible. Temperature was not controlled, but the laboratory experienced a shift of less than 4º C (17º C - 21ºC) during all experimental runs. The values of C_{in} and

C_{out} will be used to determine extent and rate of degradation of the specific NAC for each experiment.

3.6 Effect of pH

The pH of the experimental water was adjusted to determine what effects pH had on NAC reduction and byproduct formation. Phillips (2003) reported that at low pH, nitrotoluene reduction rates improved. Experiments were conducted to determine if the same trend will be seen for dinitrotoluenes (see Table 3.2). After a known molar amount of formic acid was added to 20L of DI water, the pH was adjusted with NaOH to desired levels (4.0, 5.0, 6.0). A stirplate was used to ensure complete mixing while pH adjustments were being made. After the desired pH was obtained, the mixture was stirred overnight (approx. 12 hours). The pH was measured again and recorded immediately prior to running the experiment. For each experiment, the pH of the column effluent was measured for each sample, though the influent pH was assumed constant throughout the experiment and was not measured once the experiment began.

3.7 Effect of Contaminant Concentration

Experiments were conducted at differing initial concentrations to study the effect of contaminant concentration on reduction rate and daughter products. The experiments were conducted following procedures outlined in Section 3.5 for contaminant concentrations of 20, 40, and 100 ppm (see Table 3.2). Higher contaminant

concentrations were unrealistic for groundwater contamination due to the low solubility of 2,4-DNT (270 mg/L).

3.8 Effect of Formic Acid Concentration

The experimental setup to determine the effect of formic acid concentration on NAC reduction rate and daughter products followed procedures outlined in Section 3.5. Greater degradation rate of nitrotoluenes occurred at higher formic acid concentrations (Phillips, 2003) and experiments will determine if this also applies to dinitrotoluenes. Concentrations of 1, 4, and 10 mMol of formic acid were studied (see Table 3.2).

3.9 Application of Michaelis-Menten Kinetics

When contaminant concentrations are low, a simple first-order equation can be used to model degradation,

$$\frac{dC}{dt} = -kC\,, \qquad (1)$$

where the change in contaminant concentration over time (dC/dt) is equal to the contaminant concentration (*C)* times a degradation rate constant (*k*). To obtain a value for *k,* the method outlined by Phillips (2003) will be employed. A plot of dC/dt versus C_{lm} is used to obtain the first-order rate constant. For a column experiment, we use the log mean concentration within the column (C_{lm}) (see Equation (2)) to represent the contaminant concentration (C) in Equation (1)

$$C_{lm} = \frac{C_{in} - C_{out}}{\ln(C_{in} / C_{out})} \qquad (2)$$

where C_{in} and C_{out} are the column influent and effluent contaminant concentrations, respectively. The change of contaminant concentration over time (dC/dt) is determined using Equation (3)

$$\frac{dC}{dt} = \frac{(C_{in} - C_{out})}{\theta} \qquad (3)$$

where the hydraulic retention time (θ) in minutes is calculated for each experiment as the column pore volume (69.2 mL) divided by the flowrate of water through the column in mL/min. A value close to 1 minute was used for θ in all column experiments. If kinetics are first-order, a linear regression of the dC/dt vs. C_{lm} plot results in a line whose slope is the value of k in Equation (1).

A first-order degradation rate model assumes that the only factor affecting contaminant degradation is the contaminant concentration itself; other factors that may potentially limit the rate of degradation, such as the concentration of electron donor, number of active catalyst sites, or the mass transfer rate of the contaminant to the catalyst surface are not considered. However, researchers have found that for many reactions, as the concentration of the contaminant increases, degradation rates become limited (perhaps by limitations due to electron donor or availability of catalyst sites) and first-order kinetics no longer apply. In fact, at sufficiently high contaminant concentrations, it is often found that the rate of reaction becomes constant, so reaction kinetics may be described as a zero-order process. This transition from first-order to zero-order Pd-

catalyzed degradation kinetics with increasing mononitrotoluene concentration was described by Phillips (2003) using a Michaelis-Menten model:

$$\frac{dC}{dt} = -\frac{(V_{\max})(C_{lm})}{(K_{1/2} + C_{lm})} \qquad (4)$$

Where: dC/dt = reaction rate [ppm t^{-1}]
V_{max} = maximum reaction rate [ppm t^{-1}]
$K_{1/2}$ = half-velocity constant [ppm]
C_{lm} = contaminant concentration [ppm]

We see from Equation (4) that for very low contaminant concentrations (C_{lm}), when the $K_{1/2}$ value is much larger than C_{lm}, the reaction will appear first-order with a rate constant (k) equal to $V_{max}/K_{1/2}$. As the value of C_{lm} increases, so that $C_{lm} >> K_{1/2}$, the reaction rate becomes constant with a value equal to V_{max} (Figure 3.2). Note from Figure 3.2 that $K_{1/2}$, which is referred to as the half-velocity constant, represents the substrate concentration at which the rate of substrate degradation is half of V_{max}.

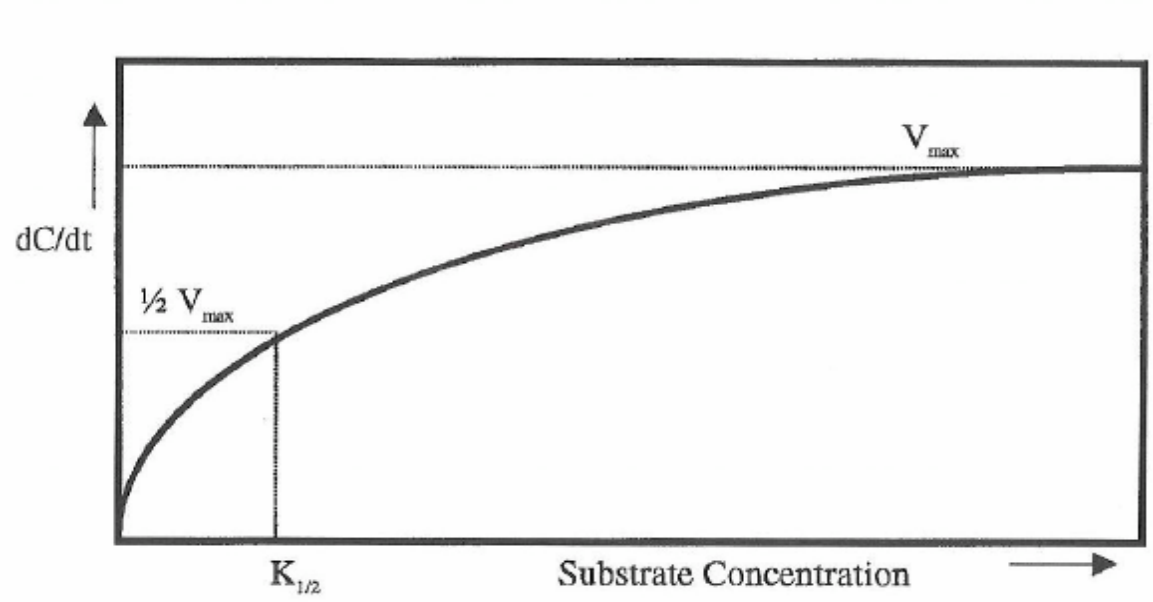

Figure 3.2 Typical Michaelis-Menten curve (Boggs, 2000)

Analysis of C_{lm} vs. dC/dt data was done using Microsoft Excel 2000 spreadsheets to store, plot, and perform linear regression to solve for first-order values of *k*. For Michaelis-Menten modeling, Axum 7, Seattle, Washington, software was used to solve best fit values for V_{max} and $K_{1/2}$.

3.10 Daughter Product Identification

The suspected daughter products of the reduction of 2,4-DNT come from previous research conducted by Neri *et al*. (1995) and Rajashekharam *et al*. (1997). Both proposed similar reduction schemes seen in Figure 2.5 and Figure 2.6, respectively. Chemical samples of each of these daughter products were obtained and calibration standards were made (see Appendix C). Reaction byproducts were identified by their residence time within the HPLC column. The typical residence time for each chemical is shown in Table 3.1 below.

HPLC Residence Times

Chemical	Time (min)
2-NT	7.57
3-NT	8.19
4-NT	7.86
2-aT	4.33
3-aT	4.33
4-aT	4.22
2A4NT	5.06
4A2NT	4.85
2,4-DAT	2.89
2,4-DNT	7.02

Table 3.1 HPLC typical residence times for contaminant chemicals studied

The separation for each chemical was sufficient to identify it by its residence time with the exception of the aminotoluene isomers (2-aT, 3-aT, 4-aT). The three aminotoluene (aT) isomers could not be separated if two or more standards were run in the same sample. However, no researchers have reported the complete removal of the nitrogen group using catalyst reduction so it is unlikely experiments conducted with 2,4-DNT will produce both 2-aT and 4-aT as byproducts. Nor is there evidence in the literature that the amino group will transfer to another carbon ie. 2-aT spontaneously becomes 3-aT. With the expected reaction schemes seen in Figure 2.6 there is sufficient separation to identify all expected byproducts.

Unknown byproducts can not be identified using the HPLC as the only data generated in an HPLC run are the residence time and peak area. With no standards to compare against, unknown byproducts can not be identified with any certainty. The use of a mass spectrometer (MS) or a nuclear magnetic resonance (NMR) is required to identify unknown chemicals.

4.0 RESULTS AND DISCUSSION

4.1 Experimental Results

Experiments using 2-NT and 2,4-DNT as model contaminants were conducted in a laboratory column. Experiments studied the effects of three parameters: pH, formic acid concentration, and contaminant concentration on the rate, extent, and byproducts of 2,4-DNT reduction, as well as investigating the effects of pH on 2-NT degradation rate, extent, and byproduct formation. Experimental results for trials listed in Table 3.2 can be found in Appendices A and B. Graphs are based on data collected after analysis of influent and effluent samples using a High Pressure Liquid Chromatograph (HPLC), as described in Chapter 3. The influent and effluent concentrations (C_{in} and C_{out} respectively) were used to calculate extent and rates of degradation and the mean contaminant concentration within the column per Section 3.9. The graphs of Degradation Rate vs. C_{lm} are given in both ppm and mMol for ease of comparison.

Complete mass balance calculations could not be made due to the presence of unknown byproducts seen during HPLC analysis. The graphs identify the percent of the total influent mass that could be accounted for in the effluent, seen in Appendix A as "% Mass Id". This percentage was calculated using the molar sum of the known byproducts compared to the molar amount of contaminant seen in the corresponding influent sample. The larger the “% Mass Id” number, the greater the percentage of mass that is accounted for. A value of 100% indicates complete mass balance for that sample. Data gathered on unknown byproducts are shown in Appendix B. Not all experiments produced

unknowns--only experiments where unknowns were observed are reported in Appendix B. As concentrations for unknowns cannot be quantified, the figures in Appendix B show the behavior of the HPLC response areas as a function of time for the unknowns, rather than plotting concentration versus time.

4.2 Effects of pH on the Rate, Extent, and Byproducts of Pd-catalyzed 2-NT Reduction

4.2.1 Effects of pH on Extent of 2-NT Degradation.

The first column experiments conducted were done with 2-NT in an effort to compare results to data reported by Phillips (2003). It was hoped that degradation rate and extent would be similar to what Phillips (2003) reported, although experimental conditions were slightly different, in that the Pd catalyst mass in the current system was 150% more (152 gm vs. 100 gm) than in the column system used by Phillips (2003). However, the data gathered in this set of experiments (Experiment #1 through #4) are of questionable value as the connections from the reservoir to the mixing chamber were not constructed properly, resulting in incomplete mixing and some short circuiting. The connections were reconstructed for Experiment #5, but no additional 2-NT experiments were conducted after Experiment #4. Thus, the data reported in Appendix A for the first four experiments are suspect due to the construction of the connections. For Experiments #2 and #3, the influent curves show relatively smooth dilution within the mixing chamber so these data were considered adequate to compare with the previous results reported by Phillips (2003).

Experimental results show that the lower values of pH result in greater removal of 2-NT, as was also seen by Phillips (2003). The removal at pH = 4.0 is only slightly greater than the removal at pH = 5.15 (see Figure 4.1). The experiment conducted at pH = 6.54 showed much greater variation in the influent concentrations (not shown) which gave rise to the erratic effluent behavior. However, it is clear from the figure that at pH = 6.54 less reduction has taken place.

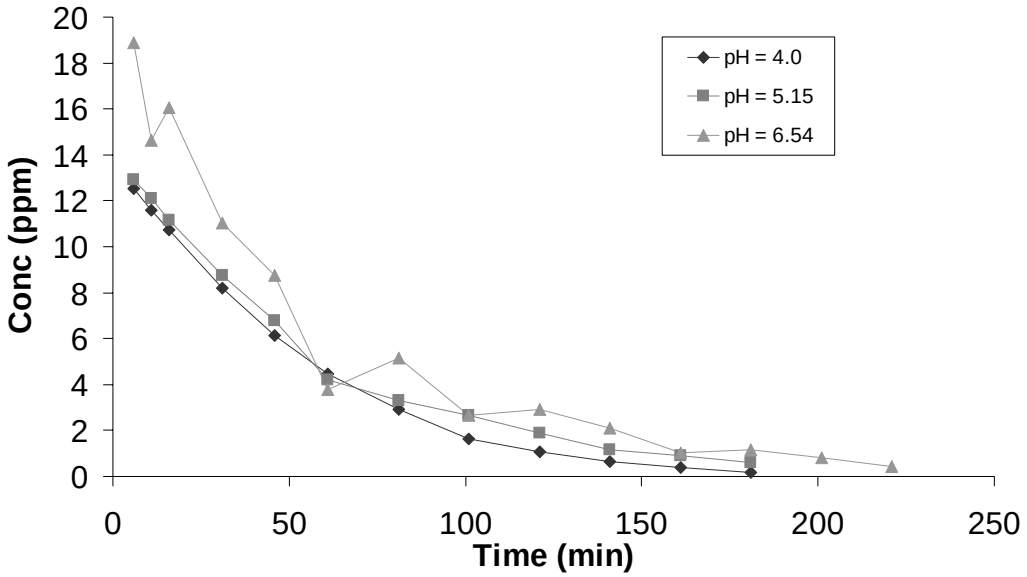

Figure 4.1 2-NT effluent concentration vs. time for differing values of pH, 20 ppm initial 2-NT concentration, 1 mMol formic acid

4.2.2 Effects of pH on 2-NT Degradation Rates.

Figure 4.2 shows that as pH is decreased, the rate of 2-NT degradation increases, which agrees with the data reported by Phillips (2003) and Prüsse and Vorlop (2001). The rate of degradation is very similar for pH = 4.0 and pH = 5.15 but there is a significant rate reduction at a pH of 6.54. The data at pH = 4.0 show Michaelis-Menten behavior with a V_{max} = 0.0719 mMol/min and $K_{1/2}$ = 0.0753 mMol. The experiment at pH = 5.15 did not produce data that can be modeled using Michaelis-Menten kinetics, so

simple linear regression was used to determine $k_1 = 0.433\ min^{-1}$. In order to compare these results with the previous work of Phillips (2003), we look at his experiment LCE #13, that was conducted under similar conditions (2-NT concentration = 45 ppm, 50 ppm of formic acid (1 mMol ≈ 46 ppm), and an influent pH of 3.43). In this experiment, Michaelis-Menten values of $V_{max} = 0.152$ mMol/min and $K_{1/2} = 0.181$ mMol were reported. To obtain an equivalent first-order rate constant for comparison purposes, divide V_{max} by $K_{1/2}$ to obtain $k_1 = 0.840\ min^{-1}$. The first-order rate constant values reported here ($k_1 = 0.433\ min^{-1}$) and by Phillips (2003) are within a factor of two, with the difference apparently due to differences in experimental conditions. The experiment at pH = 6.54 did not produce data that could be modeled due to the previously noted variations in the influent concentrations, though clearly the rates of reduction at pH = 6.54 were less than the rates at the lower pH values.

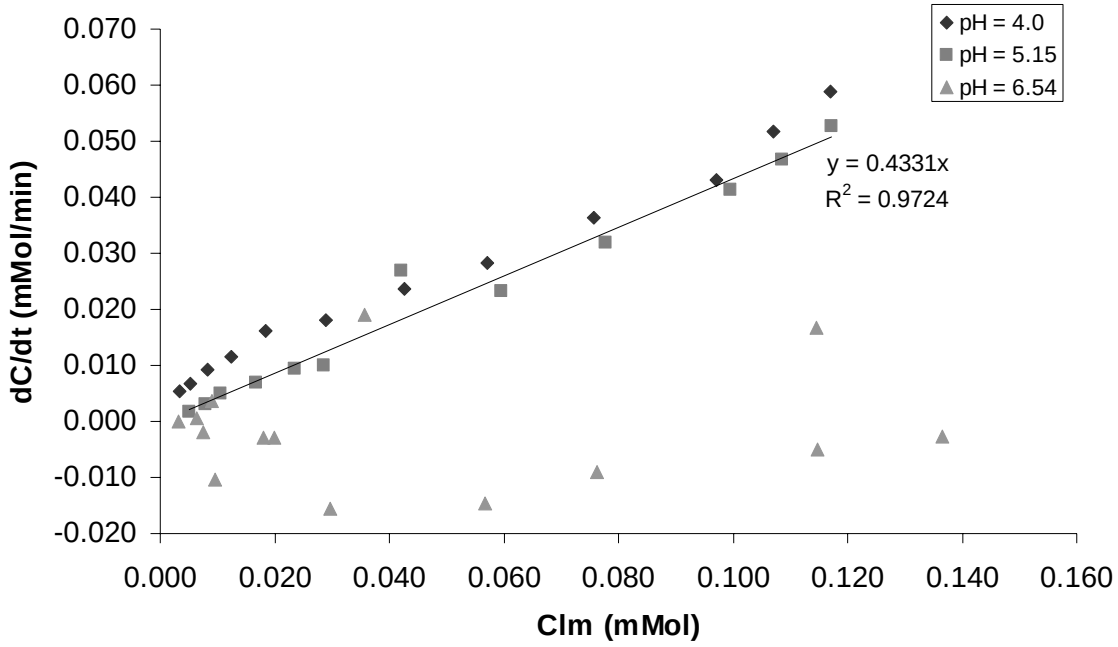

Figure 4.2 2-NT degradation rate vs. C_{lm} for differing values of pH, 20 ppm initial 2-NT concentration, 1mMol formic acid

4.2.3 Effects of pH on 2-NT Byproducts.

Reduction of 2-NT generated 2-aminotoluene (2-aT) as a byproduct for both the pH = 4.0 and pH = 5.15 experiments. The pH = 6.54 experiment did not produce any detectable 2-aT. This is most likely due to the very small amount of reduction that occurred in the higher pH experiment. The molar mass balance for these experiments, though better than for all other experiments, is not consistent and does not sufficiently account for the disappearance of all the influent 2-NT. The mass balance, based on influent 2-NT compared to effluent 2-NT and 2-aT, was between 70%-80% for the experiments at pH 4 and 5.15. The remaining unidentified mass indicates that other unidentified byproducts may result from Pd-catalyzed 2-NT reduction with formic acid as a reductant.

The concentration of the 2-aT produced was dependent on the pH of the system. A greater concentration of 2-aT was observed at pH = 4.0. However, this greater concentration may be attributed to the greater extent of reduction that occurred at the lower pH, as opposed to the reaction following an alternative pathway (which produced more 2-aT) at the lower pH. The maximum concentration of 2-aT seen was only 0.0186 mmol/L (1.99 ppm) (Exp #2, Sample 2), which occurred with an influent 2-NT concentration of 0.133 mmol/L. The total amount of 2-NT reduced at this point in the dilution experiment was 0.0485 mmol/L (0.133 mmol/L – 0.0845 mmol/L). Thus, the 2-aT accounted for approximately 38% of the 0.0485 mmol/L mass of 2-NT that was reduced.

4.3 Effects of pH on the Rate, Extent, and Byproducts of Pd-catalyzed 2,4-DNT Reduction

4.3.1 Effects of pH on Extent of 2,4-DNT Degradation.

Experiments were conducted to determine how changes in pH affected the rate of degradation for the dinitrotoluenes (see Section 3.6). Experiments were conducted at pH 4.0, 5.0, and 6.0. Samples were collected over time and analyzed for concentration of 2,4-DNT and any byproducts. In general, the amount of degradation decreased with increasing pH. This was expected, as the increased OH^- ion concentrations found at higher pHs have a negative impact on the reduction reaction by binding to catalyst sites (Prüsse and Vorlop, 2001). The effect of pH on the degradation of 2,4-DNT from Experiment #5, #6, and #7 can be seen in Figure 4.3 below.

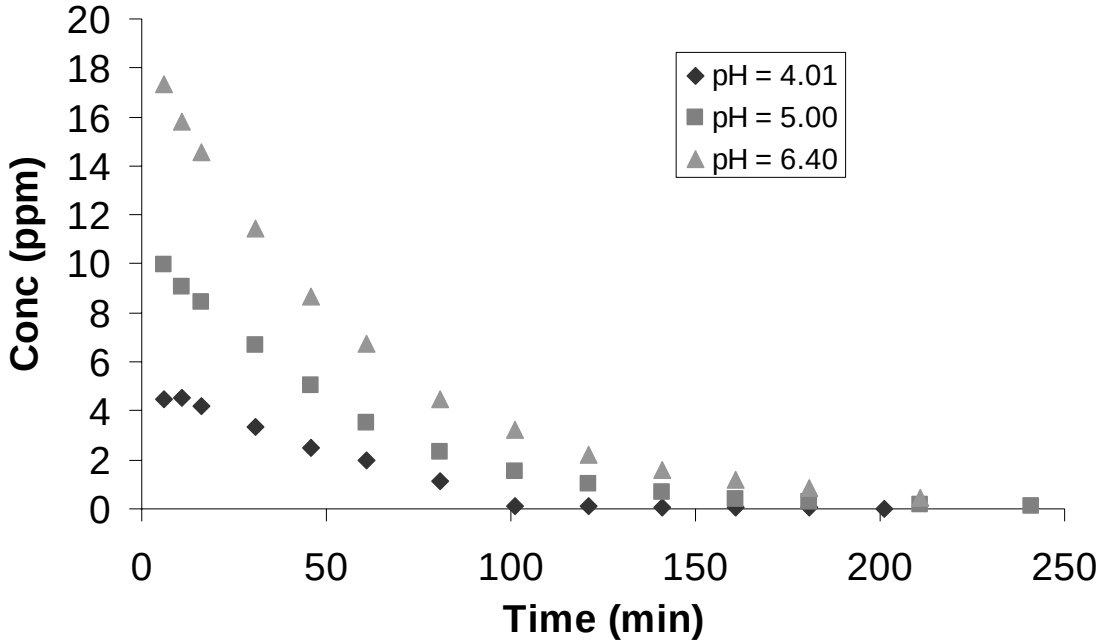

Figure 4.3 2,4-DNT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 1 mMol formic acid

With the starting concentrations equal and all other experimental parameters constant save pH, the concentration of 2,4-DNT in the effluent stream decreases with lower pH values. This agrees with information reported by Prüsse and Vorlop (2001) that palladium is deactivated at higher pHs. The trend was also observed in Section 4.2.1 with reduction of 2-NT and has been reported by Phillips (2003) for the mononitrotoluenes with Pd/Al_2O_3 catalyst. The effect of pH on degradation is observed even at higher concentrations of formic acid (donor) (Figures 4.4 and 4.5). Again, the lower values of pH result in lower concentrations of 2,4-DNT leaving the column, indicating greater amounts of reduction.

The effect of pH on degradation can be overcome with the addition of more formic acid. The higher concentration of formic acid buffers the system and the CO_2 that is produced by the degradation of formic acid removes the OH^- ions at the palladium. Also, a higher concentration of formic acid increases the availability of the electron donor so the amount of degradation and overall system performance increases. We see the effect of formic acid concentration on performance by comparing the effluent concentrations of 2,4-DNT at different pHs and formic acid concentrations. At a pH = 4.0 and 4 mMol of formic acid, initial $C_{out} \approx 5$ ppm but at pH = 6.07 and 10 mMol of formic acid, initial $C_{out} \approx 2.25$ ppm (see Figures 4.4 and 4.5). The higher pH had greater reduction due to the increased level of formic acid. Other effects of formic acid concentration will be discussed later in Section 4.4.

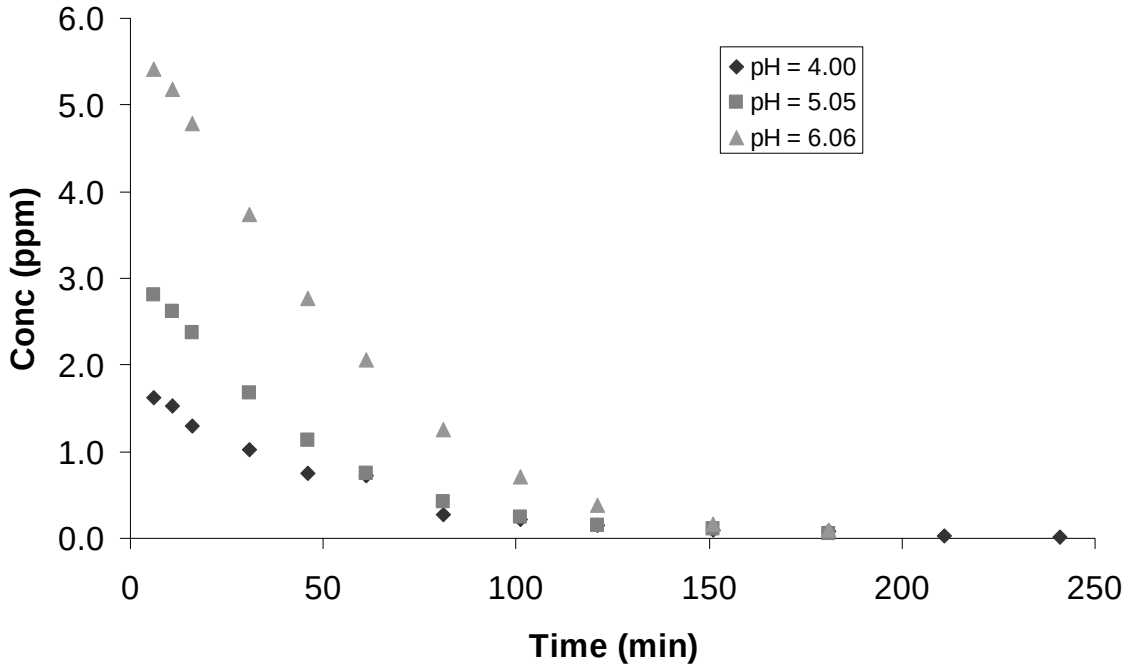

Figure 4.4 2,4-DNT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 4 mMol formic acid

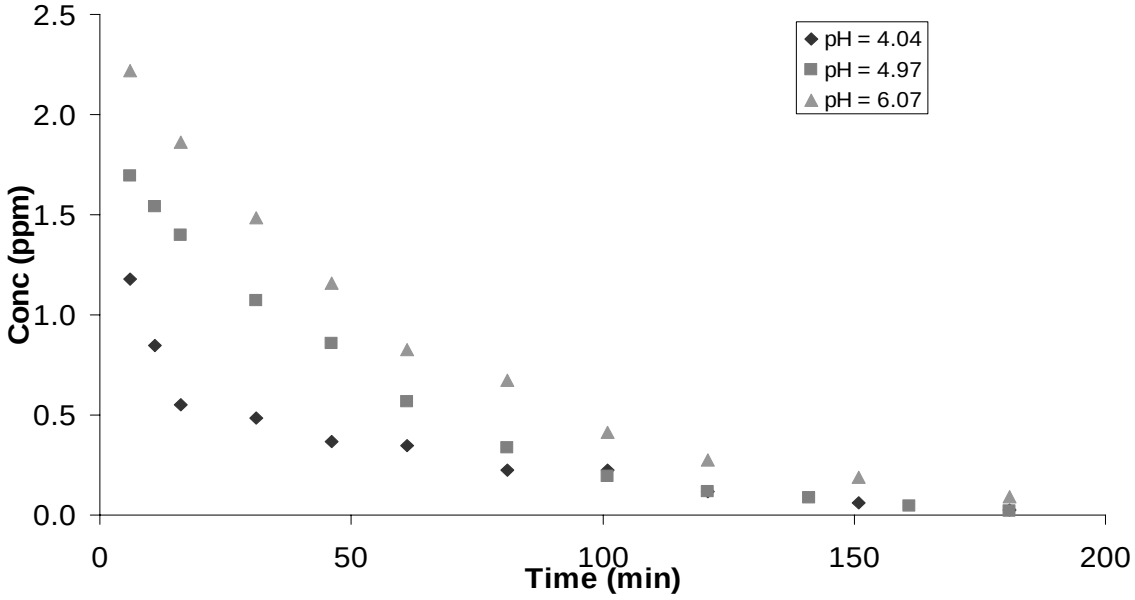

Figure 4.5 2,4-DNT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 10 mMol formic acid

4.3.2 Effects of pH on 2,4-DNT Degradation Rates.

The rate of degradation is also affected by the pH. Just as the amount of contaminant degraded increases as pH decreases, the rate of contaminant removal also increases as pH decreases. This faster rate at lower pH can again be attributed to the presence of less OH^- ions to deactivate the Pd catalyst. Results for the Degradation Rate versus the log mean 2,4-DNT Concentration (C_{lm}) for Experiments #5, #6, and #7 (shown in Figure 4.3) can be seen below in Figure 4.6.

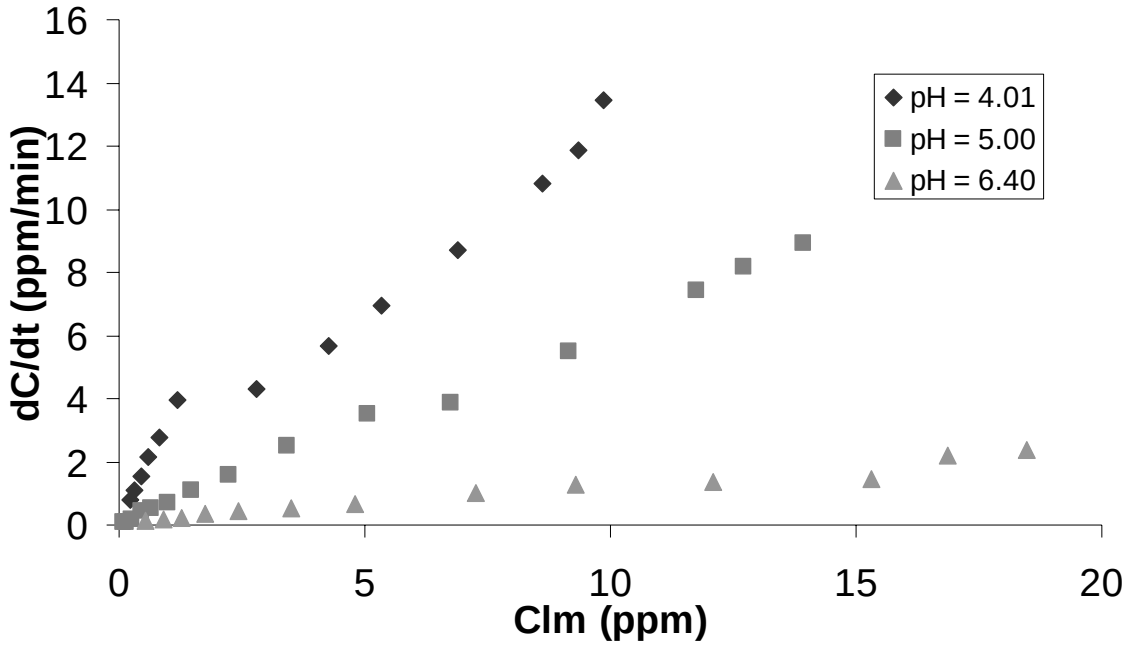

Figure 4.6 2,4-DNT degradation rate vs. C_{lm} for differing values of pH, 20 ppm initial 2,4-DNT concentration, 1 mMol formic acid

The above graph clearly shows that the lower values of pH result in much higher rates of degradation. This agrees with Prüsse and Vorlop (2001) and Phillips (2003) who reported that lower values of pH resulted in greater extents and rates of reduction. The negative effects of higher pH can also be observed at higher concentrations of formic

acid. Again, even at higher formic acid concentrations, as the pH increases, the slopes of the Degradation Rate (dC/dt) vs. C_{lm} curves decrease indicating reduced rates of degradation (see Figure 4.7 and 4.8). Note from comparing the two figures, however, that as the formic acid concentration increases, the negative impact of higher pH on performance decreases. Apparently, at high formic acid concentrations, the availability of the donor, combined with the acid's buffering capacity, reduces the negative effect of the OH^- ion on performance.

The graph of dC/dt vs. C_{lm} at a pH of 4.0 (Figure 4.6) appears non-linear. The points at very low values of C_{lm} show a linear relationship and there then is a break in the slope, followed by a second, more-or-less linear relation (with a less steep slope) between dC/dt and C_{lm} at higher values of C_{lm}. This curve does not display Michaelis-Menten type kinetics. This unusual behavior may be explained by conditions at the start of the experiment. When the experiment began the column was flushed with water containing formic acid but no contaminant. This allowed formic acid to bind to the palladium in the column. At this point, the system is primed to reduce a great amount of contaminant. As the high initial concentrations of contaminant moved through the column, the excess formic acid was consumed. It was only after the consumption of the formic acid that was initially present in the column was there confidence that effluent contaminant concentrations reflected conditions related to the influent formic acid concentration. Thus, it was deemed necessary to remove some of the initial data points, which, based on the dilution experiment methodology, are the high concentration points on the curve, to ensure that the analysis of effluent concentration data was not confounded by the formic acid initially present in the column. Individual data points were not used for curve-fitting

based on the investigator's opinion of which points exhibited anomalous behavior. All data are shown in Appendix A. After removal of the anomalous data points, some curves appeared to exhibit Michaelis-Menten kinetic behavior. Other experiments exhibited linear behavior. Kinetic values for experiments whose data exhibit Michaelis-Menten behavior can be found in Table 4.1 and for experiments whose data exhibit linear behavior in Table 4.2.

The higher concentrations of formic acid (10 mMol) appeared to produce first-order results for Degradation Rate vs. C_{lm} plots at higher values of pH (Figure 4.8). When the formic acid concentration was not as high (4 mMol) reduction rate appeared limited by the electron donor, especially at high pH (Figure 4.7). Figure 4.7 shows that the Degradation Rate vs. C_{lm} curves for different pHs exhibit Michaelis-Menten behavior; they appear linear at low 2,4-DNT concentrations, with slowly decreasing slopes at higher concentrations. At these higher concentrations, either electron donor or available catalyst sites may be limiting 2,4-DNT reduction.

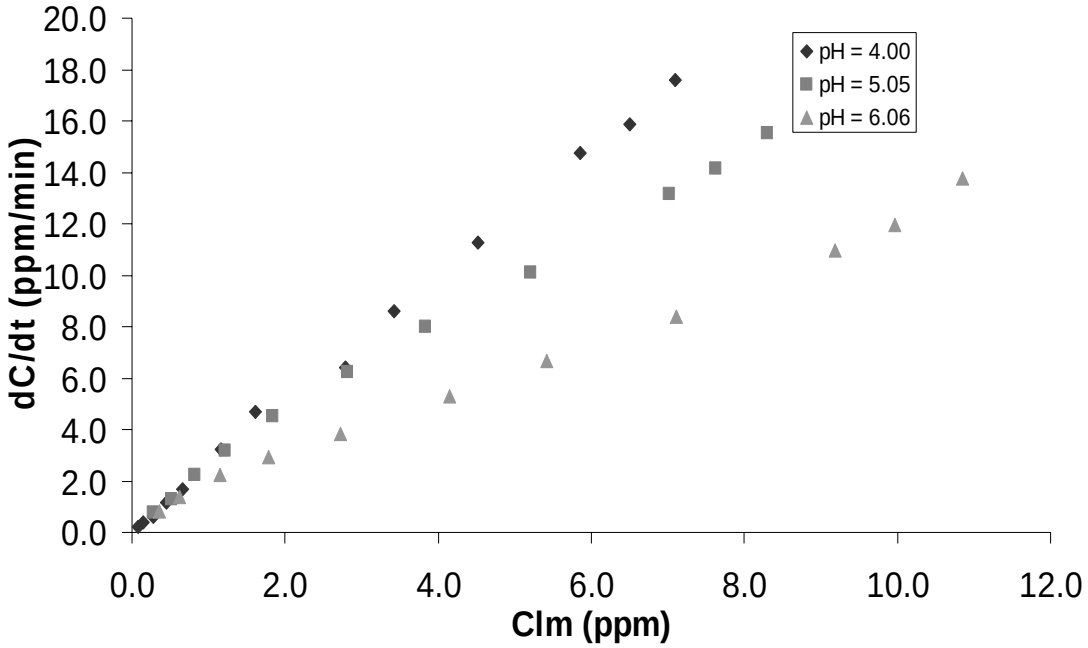

Figure 4.7 2,4-DNT degradation rate vs. C_{lm} for differing values of pH, 20 ppm initial 2,4-DNT concentration, 4 mMol formic acid

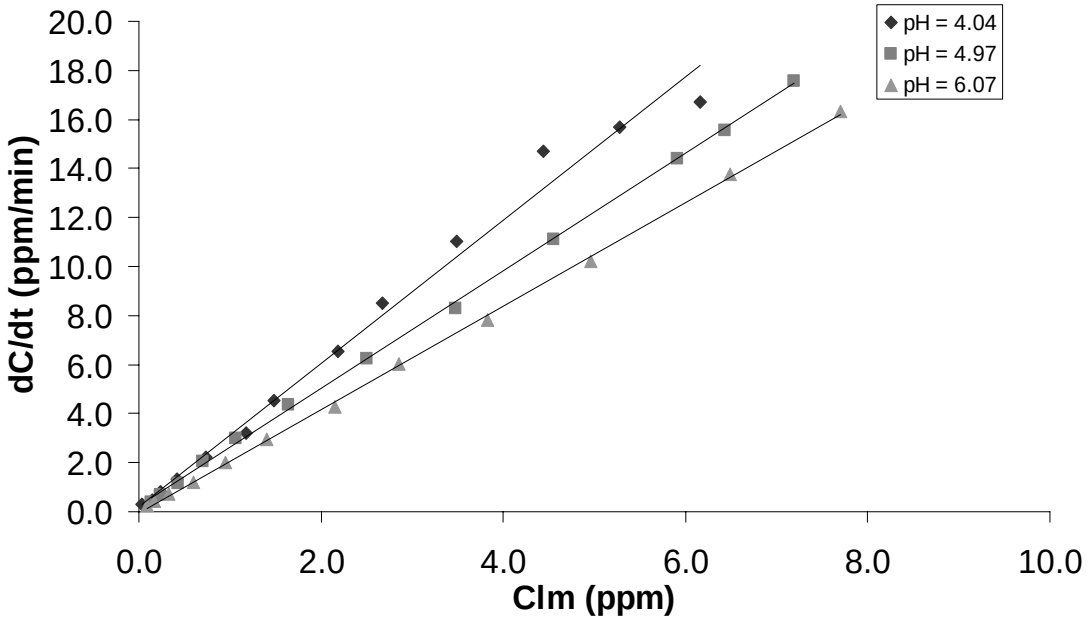

Figure 4.8 2,4-DNT degradation rate vs. C_{lm} for differing values of pH, 20 ppm initial 2,4-DNT concentration, 10 mMol formic acid

Experiment Number	Contaminant	Initial Conc (ppm)	Formic Acid (mMol)	pH	Kinetic Parameters V_{max} = mMol/min K = mMol
2	2-NT	20	1.0	3.99	V_{max} = 0.0718974 K = 0.0752570 correlation = 0.978
5	2,4-DNT	20	1.0	4.01	V_{max} = 0.0638136 K = 0.0183905 correlation = 0.953
7	2,4-DNT	20	1.0	6.40	V_{max} = 0.0163293 K = 0.0793023 correlation = 0.983
13	2,4-DNT	20	4.0	5.06	V_{max} = 0.1684350 K = 0.0590204 correlation = 0.995
14	2,4-DNT	20	4.0	6.06	V_{max} = 0.1211080 K = 0.0670712 correlation = 0.994
15	2,4-DNT	20	10.0	4.04	V_{max} = 0.501960 K = 0.142396 correlation = 0.999
20	2,4-DNT	40	4.0	4.00	V_{max} = 0.797930 K = 0.248874 correlation = 0.999
21	2,4-DNT	40	1.0	4.00	V_{max} = 0.1263130 K = 0.0924327 correlation = 0.984
23	2,4-DNT	100	1.0	4.00	V_{max} = 0.364384 K = 0.593804 correlation = 0.996
24	2,4-DNT	100	1.0	5.05	V_{max} = 0.312861 K = 0.780152 correlation = 0.998

Table 4.1 Column experiments (results exhibit Michaelis-Menten kinetic behavior)

4.3.3 Effects of pH on 2,4-DNT Byproducts.

pH does have an effect on the formation of intermediate byproducts. When the pH was near 4.0 there was limited formation of both 2-amino, 4-nitrotoluene (2A4NT) and 4-amino, 2-nitrotoluene (4A2NT) compared to formation at higher values of pH (see Figures 4.9 and 4.10). These two intermediates can be observed in the reduction pathways proposed by both Neri *et al*. (1995) and Rajashekharam *et al*. (1997) (Figures 2.5 and 2.6).

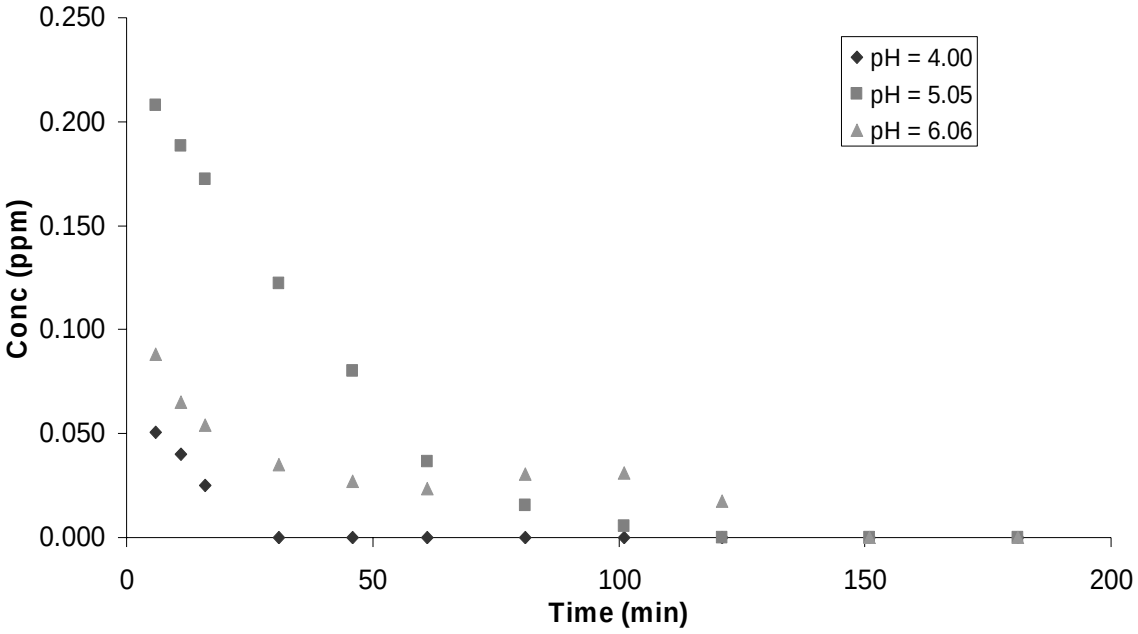

Figure 4.9 2A4NT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 4 mMol formic acid

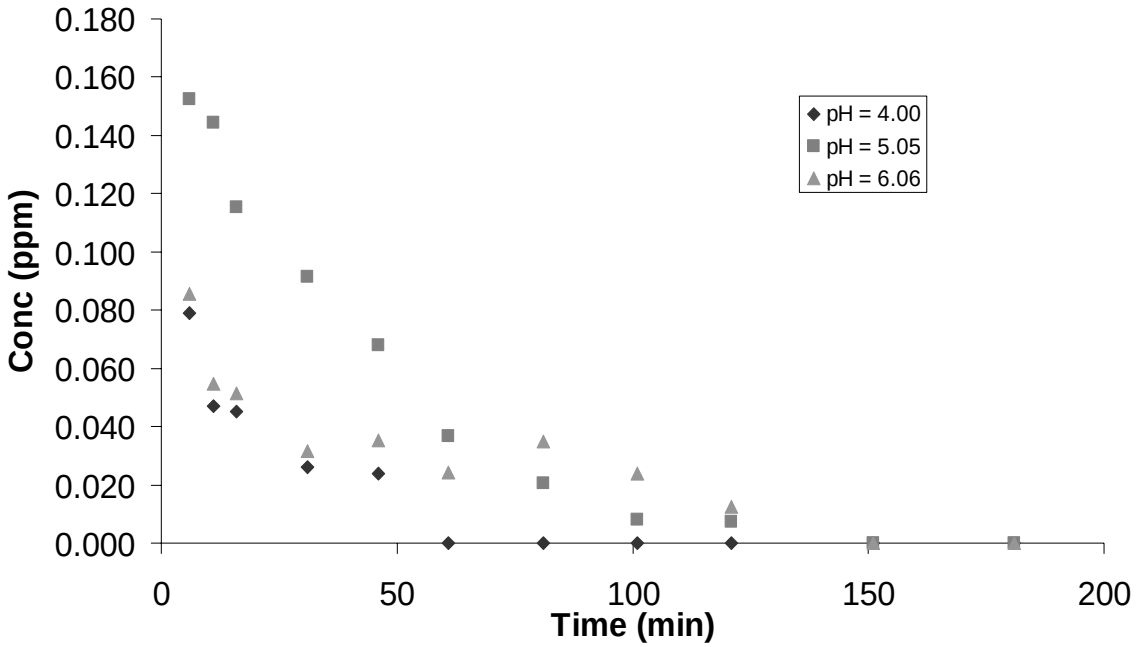

Figure 4.10 4A2NT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 4 mMol formic acid

At low pH, intermediate byproduct production is reduced. This could be attributed to faster rates of degradation at lower pH values for the intermediates as seen in Section 4.2.1. The lower concentration of intermediates at pH = 6.0 can be attributed to less overall reduction in the system at the higher pH. The data again indicate further reduction may be taking place. At pH = 4.0, greater overall reduction was observed, but byproduct concentrations are less than at pH = 5.0 where less overall reduction occurred.

At a lower pH and low concentrations of formic acid (1 mMol), greater amounts of 2,4-diaminotoluene (2,4-DAT) were produced than at higher pH (see Figure 4.11). However, at higher concentrations of formic acid (10 mMol), this was not observed, and 2,4-DAT concentrations were relatively independent of pH (see Figure 4.12). It is more likely that the 2,4-DAT levels were higher at all pHs when more reductant was present

due to the increased overall degradation, rather than a relationship between low pH and increased 2,4-DAT formation. At higher concentrations of formic acid (10 mMol) the extent and rate of degradation were similar (Figures 4.5 and 4.8) and pH had a limited affect on the system. The similar extent and rate of degradation should lead to similar concentrations of byproducts unless the different pHs cause a preference for a reduction pathway. At a pH of 4.0 there was less intermediate observed but at a pH of 5.0 and 6.0 both 2A4NT and 4A2NT concentrations were comparable (data not shown). Figure 4.12 illustrates that the amount of 2,4-DAT produced is consistent regardless of the pH indicating the amount of reduction, not the pH directly, affects byproduct formation.

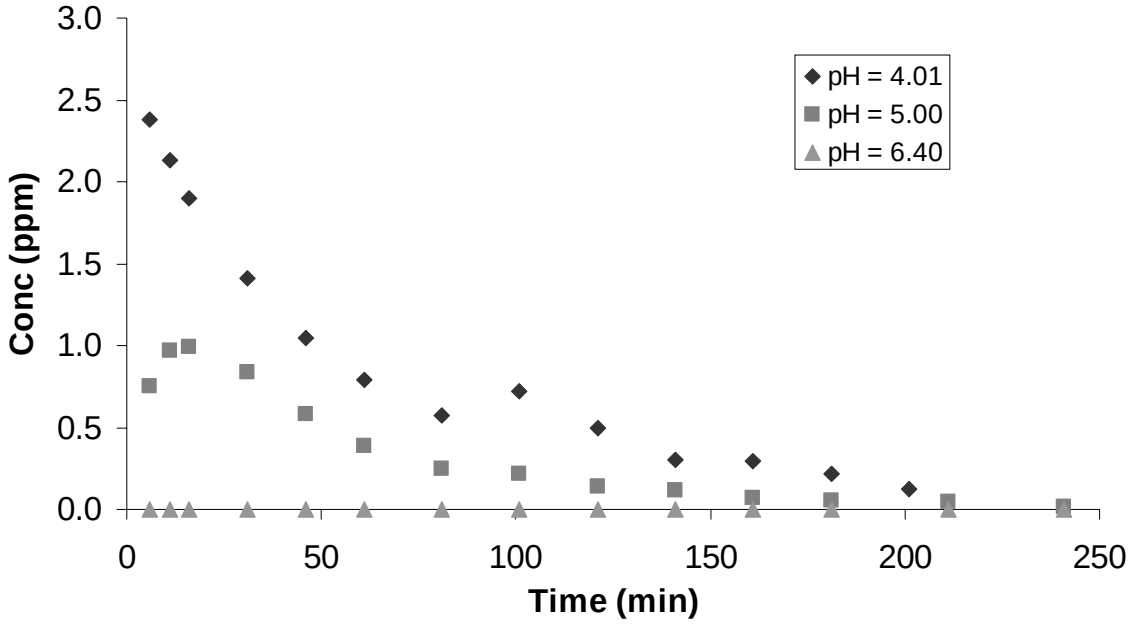

Figure 4.11 2,4-DAT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 1 mMol formic acid

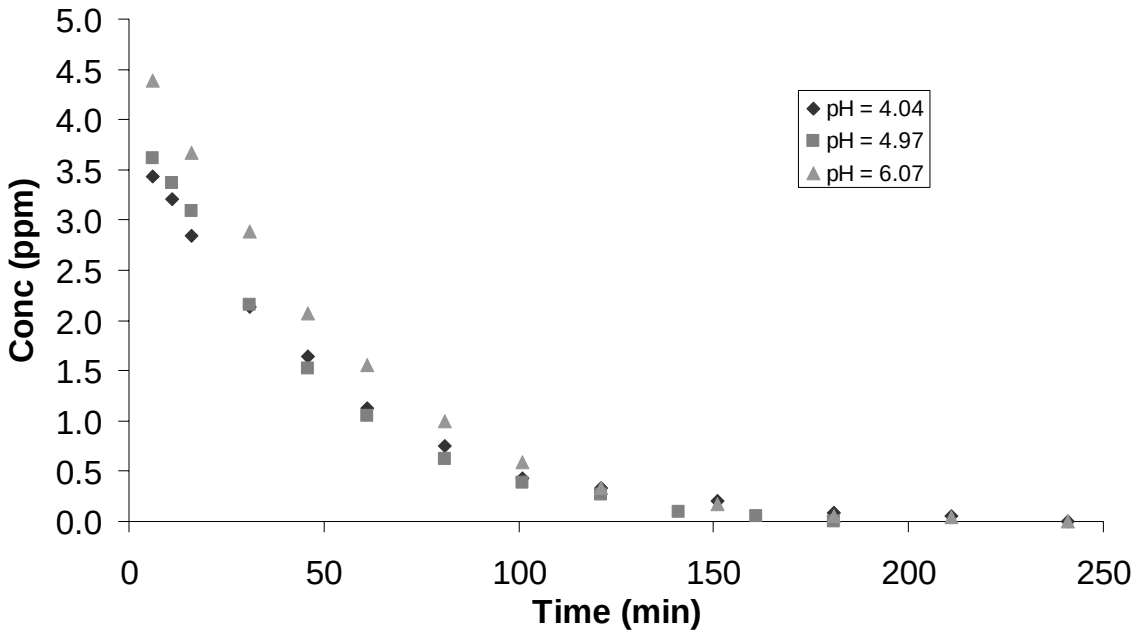

Figure 4.12 2,4-DAT effluent concentration vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 10 mMol formic acid

4.4 Effects of Formic Acid on the Rate, Extent, and Byproducts of Pd-catalyzed 2,4-DNT Reduction

4.4.1 Effects of Formic Acid on Extent of 2,4-DNT Degradation.

Column experiments were conducted to study the effect of formic acid concentration on system performance (see Table 3.2). Concentrations of 1, 4, and 10 mMol of formic acid were used. For 2-NT, Phillips (2003) found that as the concentration of formic acid increased, the degradation increased. This was due to an increased amount of electron donor, as well as formic acid's ability to buffer the system, preventing a pH increase that would have a detrimental effect on performance. The results obtained for column experiments with 2,4-DNT are in agreement with previous results; that is, contaminant reduction increased at higher concentrations of formic acid.

This may be observed when effluent concentrations of 2,4-DNT are plotted versus time (Figure 4.13a, b). The higher the formic acid concentration, the lower the effluent contaminant concentration indicating more removal has taken place.

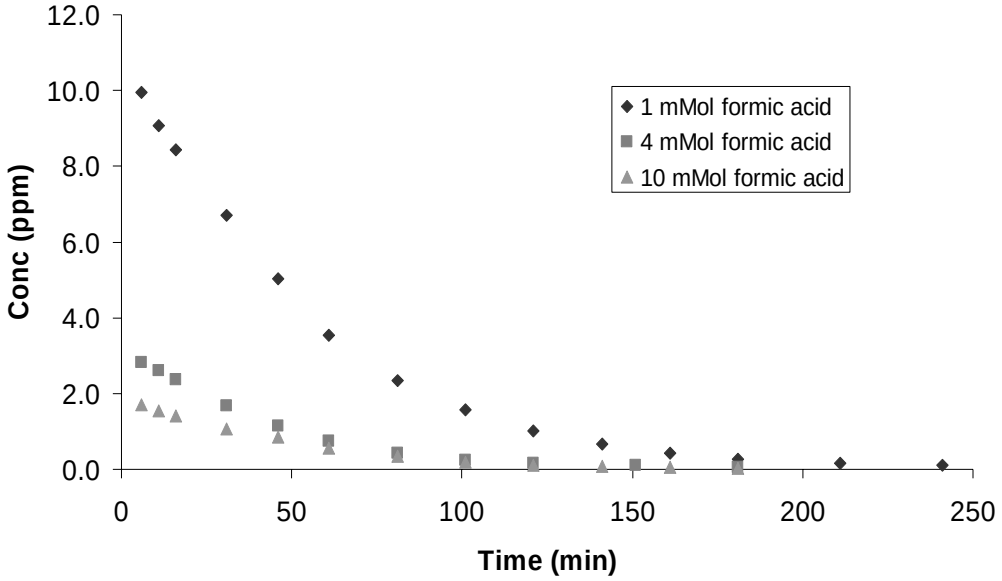

Figure 4.13a 2,4-DNT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 5.0

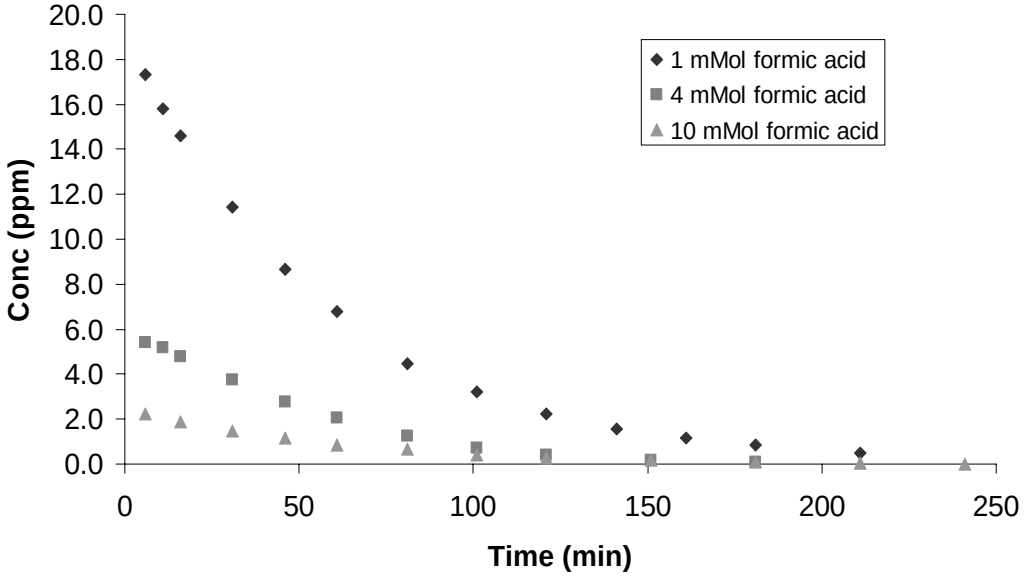

Figure 4.13b 2,4-DNT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 6.0 - 6.4

The effect of formic acid on the system can be seen at differing values of pH by comparing Figures 4.13a with 4.13b. At a pH of 5.0 and a pH of 6.0 the trend is the same, higher formic acid concentrations result in lower effluent concentrations of 2,4-DNT, indicating greater reduction. However, this behavior of increasing reduction with increasing reductant concentration is only true when reductant is limiting. In Figure 4.14, which shows effluent concentrations for pH = 4.0 and increased initial influent 2,4-DNT concentration, we see there is little difference in 2,4-DNT effluent concentration between 4 and 10 mMol formic acid. This indicates that at the low pH and relatively high reductant and contaminant concentrations, reduction in the system is limited by a factor other than reductant: perhaps available catalyst sites, diffusion limitations, or residence time. The implication is that for some situations, increasing the amount of electron donor may not lead to increased degradation.

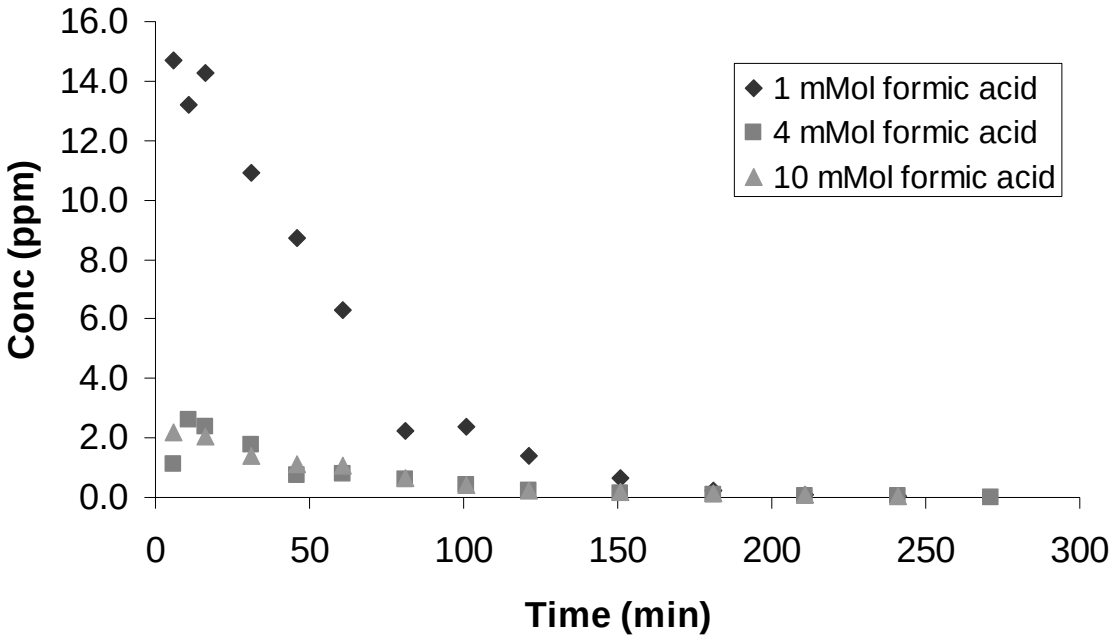

Figure 4.14 2,4-DNT effluent concentration vs. time for differing concentrations of formic acid, 40 ppm initial 2,4-DNT concentration, pH = 4.0

4.4.2 Effects of Formic Acid on 2,4-DNT Degradation Rates.

As the formic acid concentration increases from 1 to 4 to 10 mMol, while other parameters are held constant, the rate of degradation increases (Figure 4.15, 4.16, and 4.17). All three figures show that at low 2,4-DNT concentrations (< 2 ppm) the degradation rates at 4 and 10 mMol of formic acid are similar. With a pH of 4.0 and low 2,4-DNT concentrations, the degradation rates for all three formic acid concentrations are similar (Figure 4.15) indicating that for low contaminant concentrations and low pH, the reductant is not limiting, and that kinetics are first-order. As the 2,4-DNT concentration increases, the degradation rates begin to diverge, indicating that formic acid begins to limit the degradation rate. The data indicate that for systems with low levels of contaminant (< 2 ppm), increasing the amount of formic acid (electron donor) may not result in increased contaminant removal.

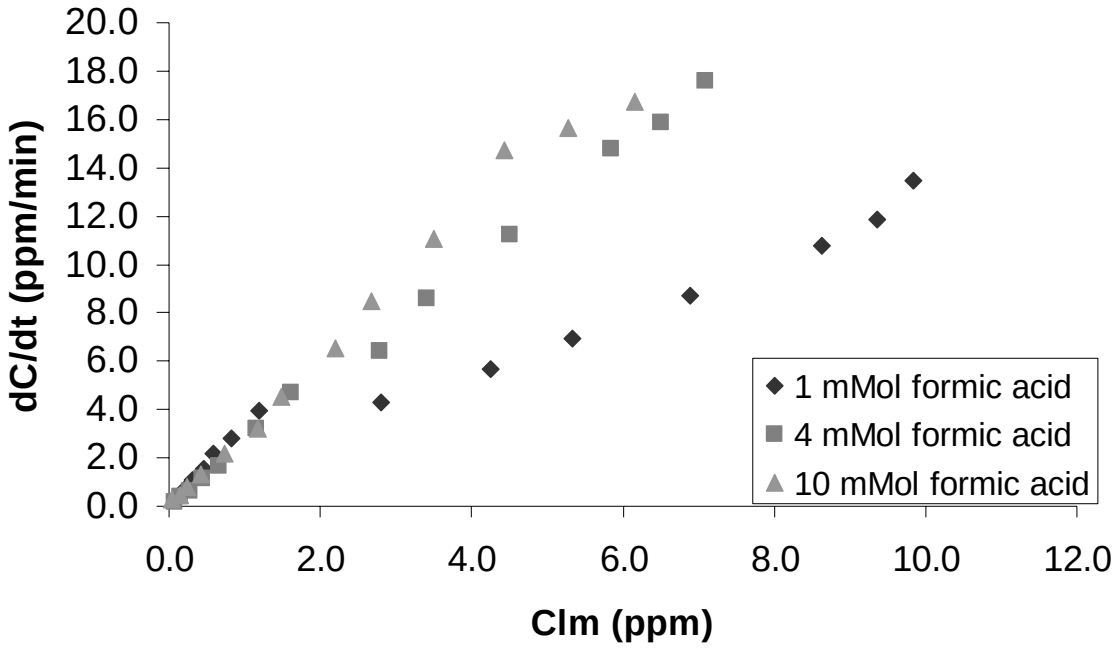

Figure 4.15 2,4-DNT degradation rate vs. C_{lm} for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 4.0

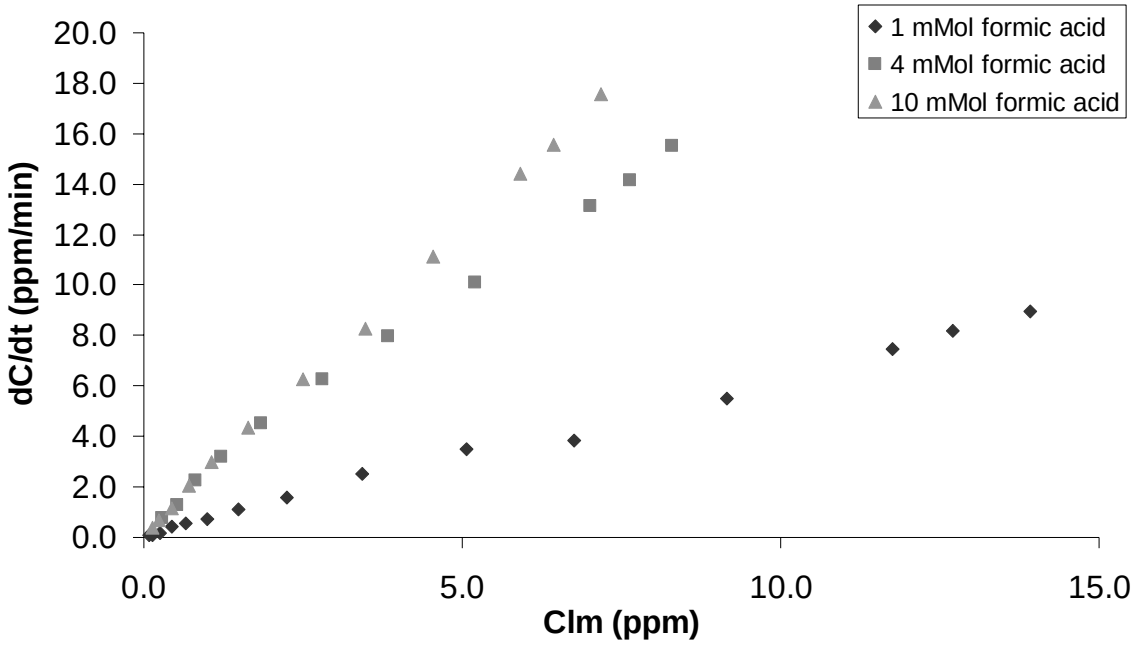

Figure 4.16 2,4-DNT degradation rate vs. C_{lm} for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 5.0

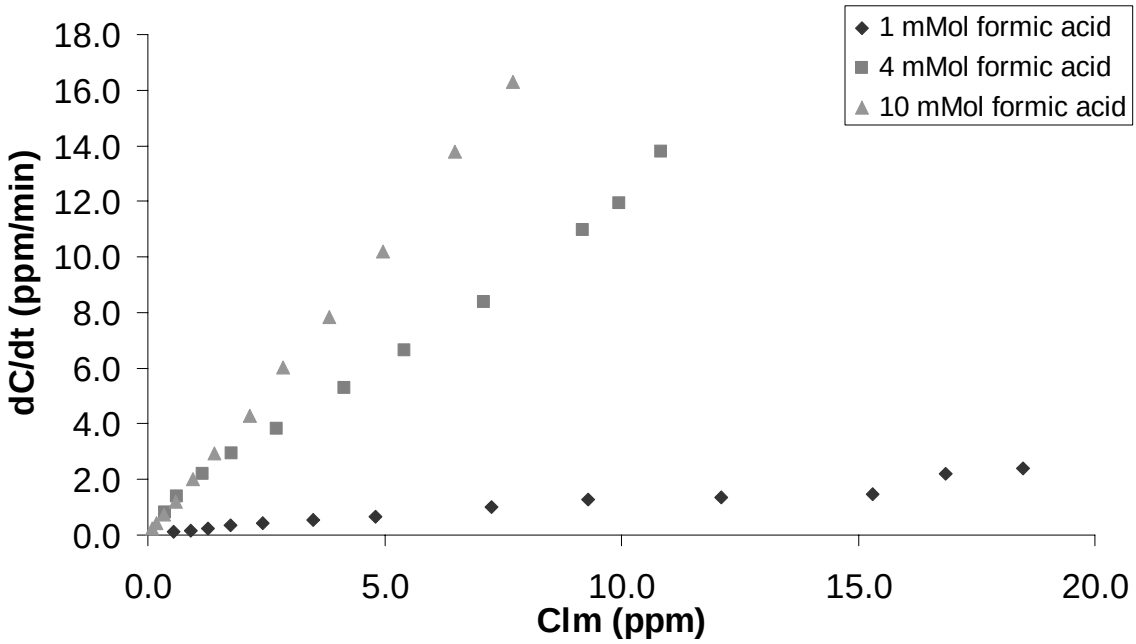

Figure 4.17 2,4-DNT degradation rate vs. C_{lm} for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 6.0

4.4.3 Effects of Formic Acid on 2,4-DNT Byproducts.

The concentration of formic acid had a significant impact on the formation of 2,4-DAT as a byproduct. Though the formation of 2,4-DAT was similar for the 4 and 10 mMol experiments, experiments using only 1 mMol of formic acid produced significantly less 2,4-DAT (Figure 4.18, 4.19, 4.20). Much of this difference can be attributed to the lower degradation rates in the 1mMol experiments. The amount of 2,4-DAT produced appears to be proportional to the initial concentration of 2,4-DNT.

In Figure 4.18 and Figure 4.21 the data show a relationship between the influent 2,4-DNT concentration and the concentration of 2,4-DAT that is produced as a byproduct. This relationship indicates that a doubling of the initial 2,4-DNT concentration led to an approximate doubling of the 2,4-DAT byproduct when all other parameters were held constant. This could have implications for site remediation as byproduct formation could be estimated based on the influent concentration. The reduction pathways in Figure 2.5 show 2,4-DAT as the final product with no further reduction expected. The amount of 2,4-DAT could be used as an indicator of system performance. If small concentrations of byproduct are seen, it could indicate the system is not operating properly or another limiting factor is affecting the remediation.

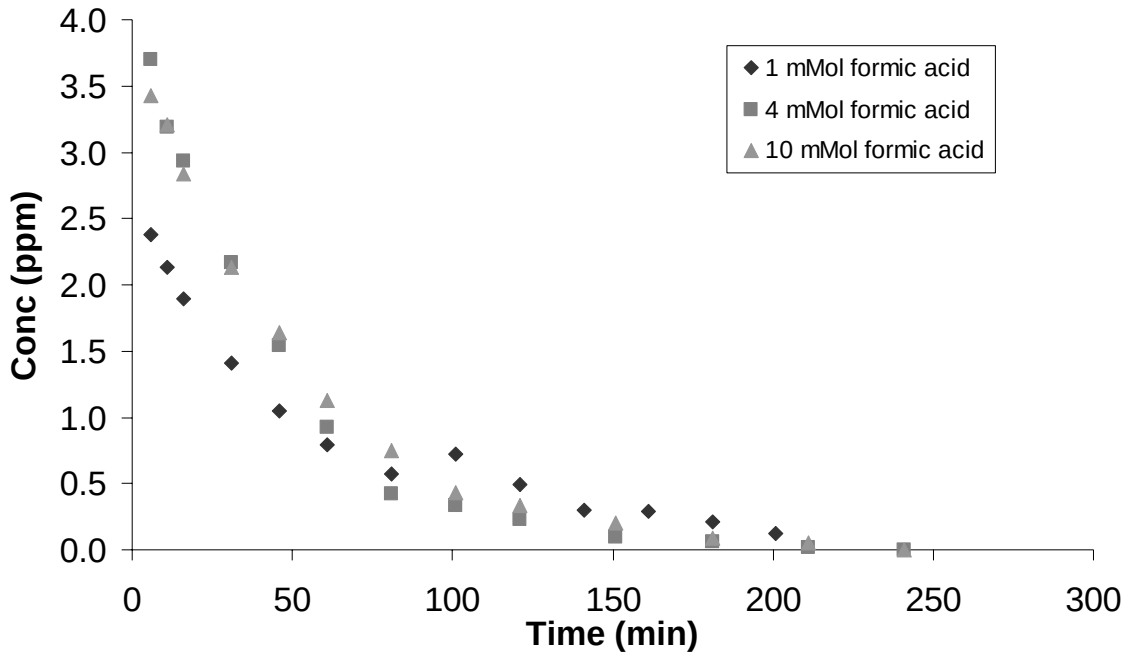

Figure 4.18 2,4-DAT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 4.0

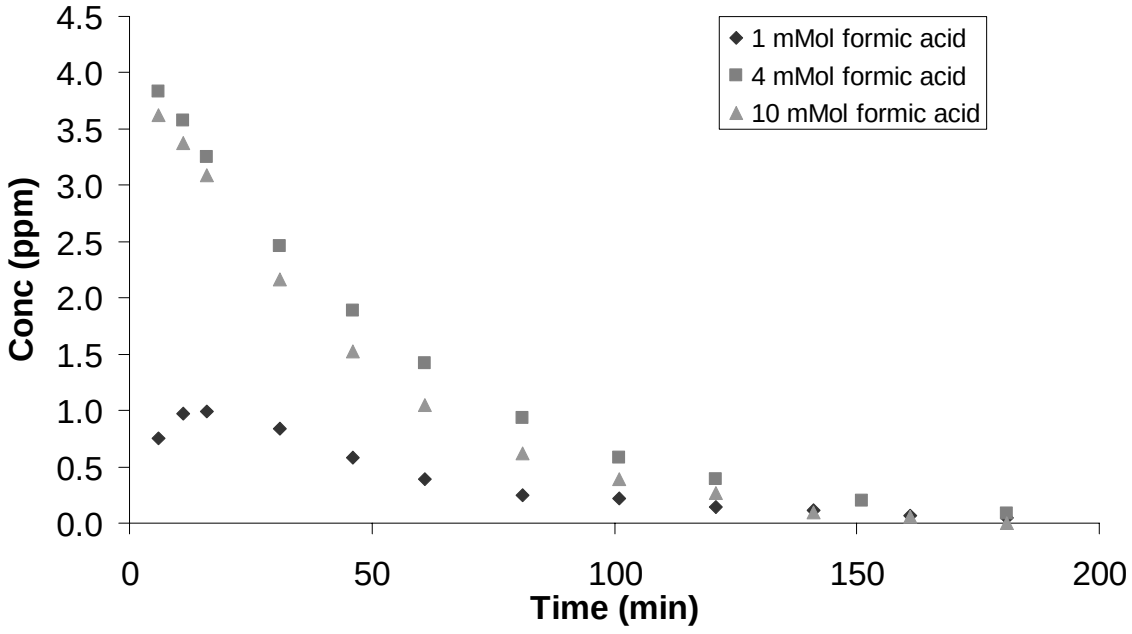

Figure 4.19 2,4-DAT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 5.0

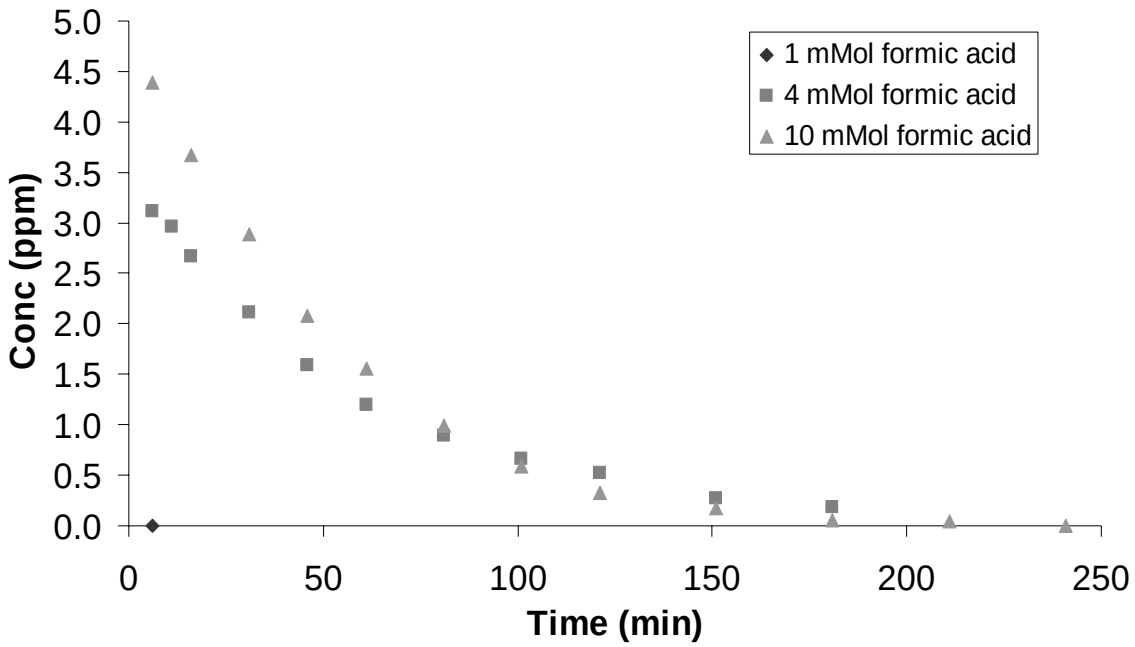

Figure 4.20 2,4-DAT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 6.0

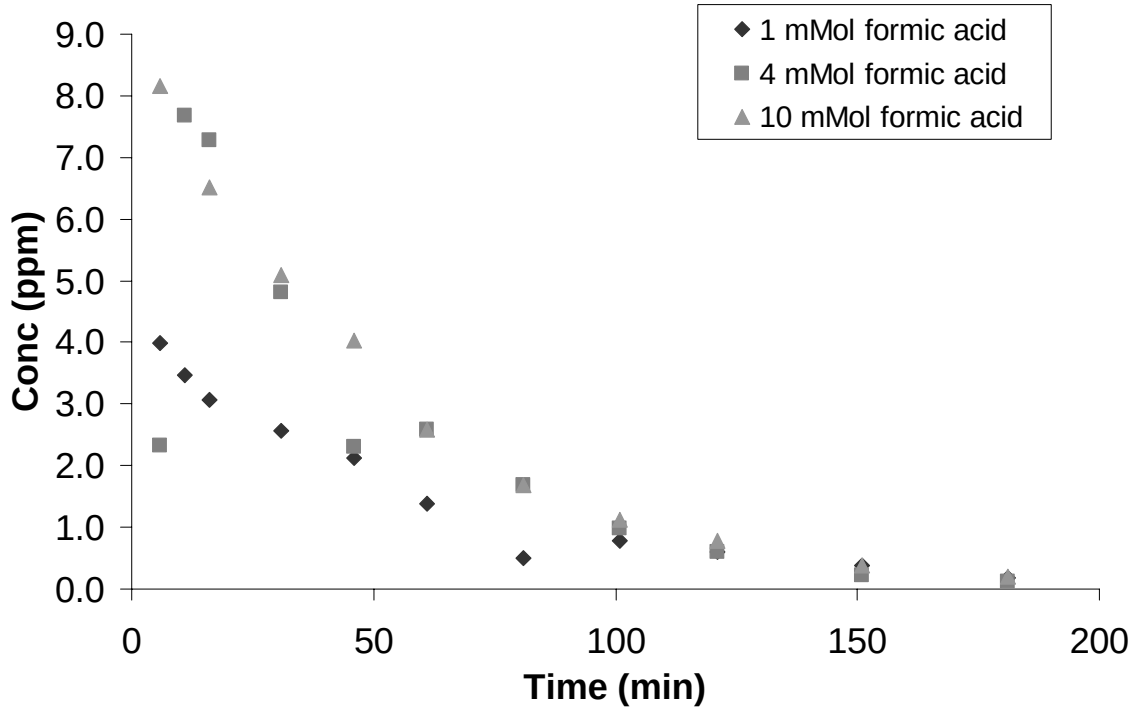

Figure 4.21 2,4-DAT effluent concentration vs. time for differing concentrations of formic acid, 40 ppm initial 2,4-DNT concentration, pH = 4.0

The relation between the production of 2A4NT and 4A2NT and formic acid concentration is shown in Figures 4.22 and 4.23. While Figure 4.23 indicates that formic acid concentration does not have an effect on 4A2NT production, there does appear to be a relationship between 2A4NT production and formic acid concentration. At lower values of pH (pH < 6.0) more 2A4NT was formed at 4 mMol of formic acid than at 10 mMol of formic acid (Figure 4.22). We saw earlier that experiments conducted at 4 mMol formic acid exhibited Michaelis-Menten behavior and speculated that formic acid became rate limiting. The greater concentrations of 2A4NT in the 4 mMol formic acid experiments may be due to the limited amount of formic acid in the system. At 10 mMol the formic acid is not limiting so intermediates were able to be reduced to 2,4-DAT. Experiments conducted with 1 mMol formic acid did not produce these intermediates in detectable quantities when the initial concentration of 2,4-DNT was 20 ppm (Figure 4.22). At greater concentrations of 2,4-DNT, all three concentrations of formic acid produced 2A4NT and 4A2NT. Byproduct production graphs for all experiments can be found in Appendix A.

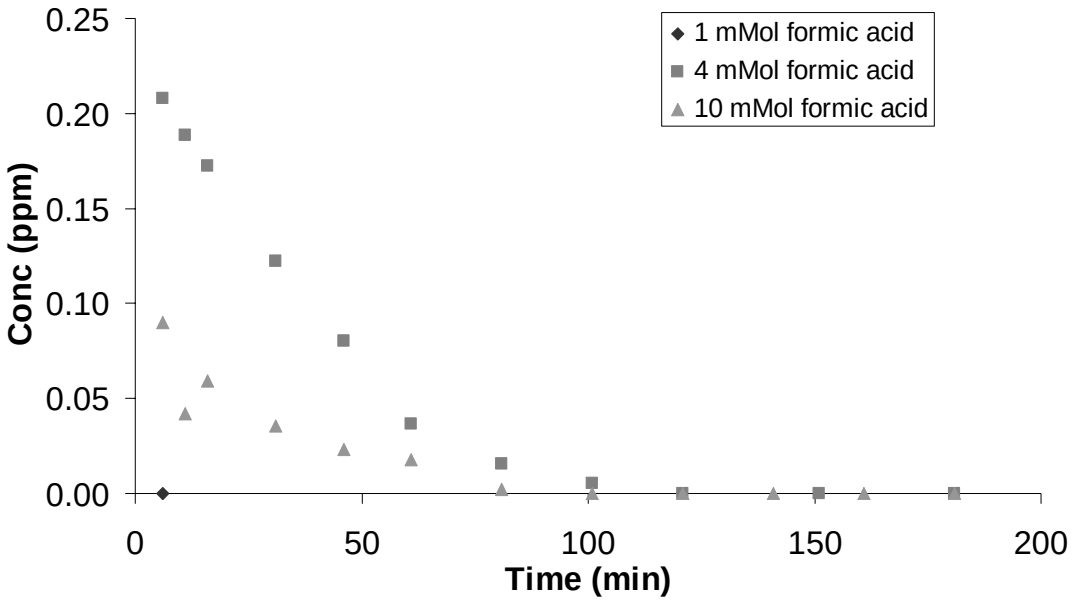

Figure 4.22 2A4NT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 5.0

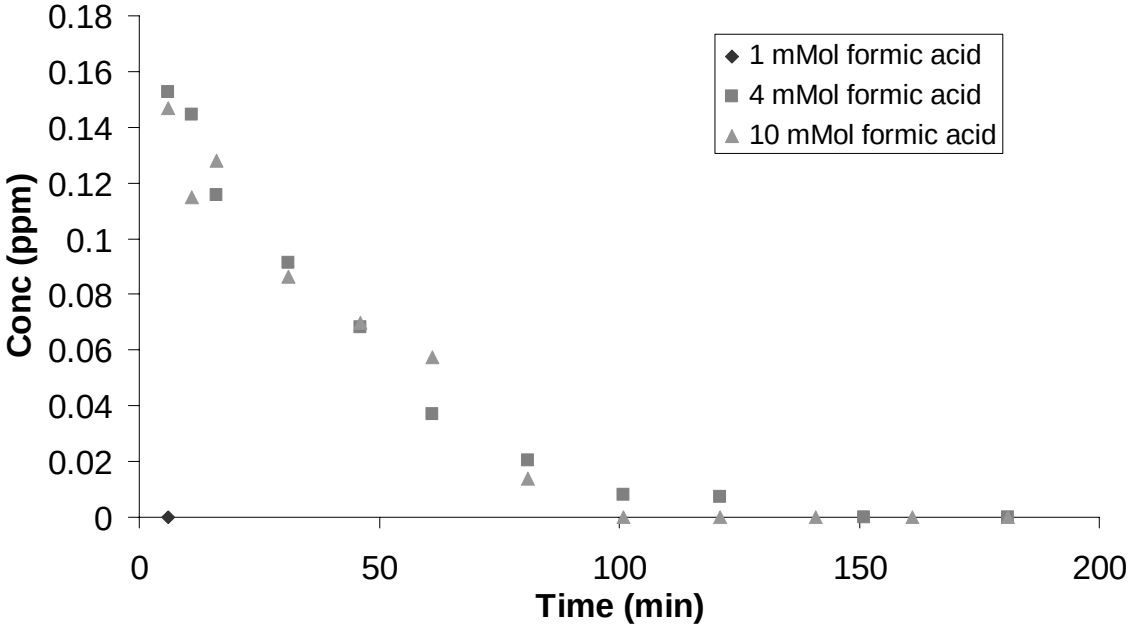

Figure 4.23 4A2NT effluent concentration vs. time for differing concentrations of formic acid, 20 ppm initial 2,4-DNT concentration, pH = 5.0

4.5 Effects of 2,4-DNT Initial Concentration on the Rate, Extent, and Byproducts of Pd-catalyzed 2,4-DNT Reduction

4.5.1 Effects of 2,4-DNT Initial Concentration on Extent of 2,4-DNT Degradation.

Experiments were conducted at differing initial concentrations of 2,4-DNT to determine the effects contaminant concentration would have on the extent of degradation. Three different 2,4-DNT initial concentrations were studied, 20, 40 and 100 ppm while all other parameters were held constant. The experiments showed that at lower concentrations of 2,4-DNT, greater removal took place as shown by Figure 4.24. The removal fraction improves over time as the influent concentration decreases due to the dilution in the mixing chamber.

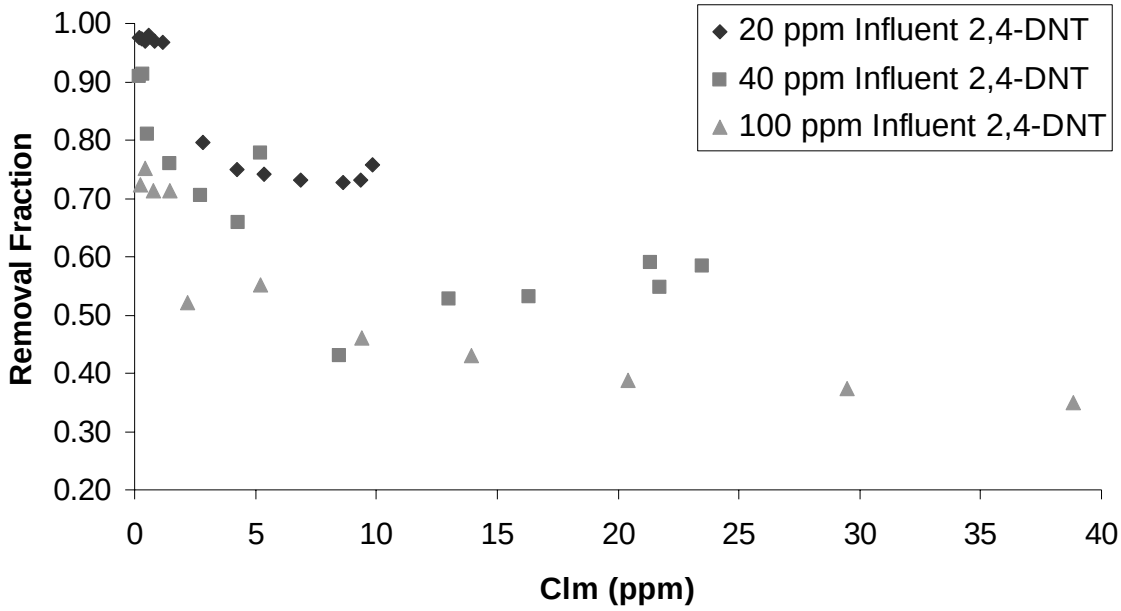

Figure 4.24 2,4-DNT removal fraction vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0 (Note: data for 100 ppm experiment not shown above 40 ppm)

Greater fraction removal was expected at lower influent concentrations due to the limited amount of palladium catalyst or electron donor (formic acid). As the influent

concentration increases, the amount of catalyst or electron donor becomes limiting. The results seen in Figure 4.24 indicate that catalyst performance is degraded by high concentrations of contaminant. At similar values of C_{lm} system performance is not the same for different initial values of 2,4-DNT. The concentration of formic acid is the same for each experiment, indicating catalyst deactivation is responsible for the smaller reductions seen at higher initial concentrations. The number of available sites has decreased, possibly due to OH^- inhibition, reducing the efficiency of the catalyst and the overall system. When the amount of contaminant exceeds the available number of sites it is possible for 2,4-DNT to pass through the column and not be reduced because catalyst sites or reductant is limiting. The results from Experiment #11 clearly indicate that 2,4-DNT is reduced only in the presence of an electron donor. In this experiment, no formic acid was added, and no reduction of 2,4-DNT occurred.

4.5.2 Effects of 2,4-DNT Initial Concentration on 2,4-DNT Degradation Rates.

The different initial influent concentrations also had an effect on the rate of degradation. The rate of degradation was highest for the 20 ppm experiment at the same values of C_{lm}, and the 40 ppm experiment was higher than the 100 ppm experiment (Figure 4.25). This is perhaps due to catalyst deactivation caused by the higher initial contaminant concentration. Figure 4.26 expands the low C_{lm} portion of Figure 4.25 and clearly indicates the higher degradation rates observed at the lower initial 2,4-DNT concentrations.

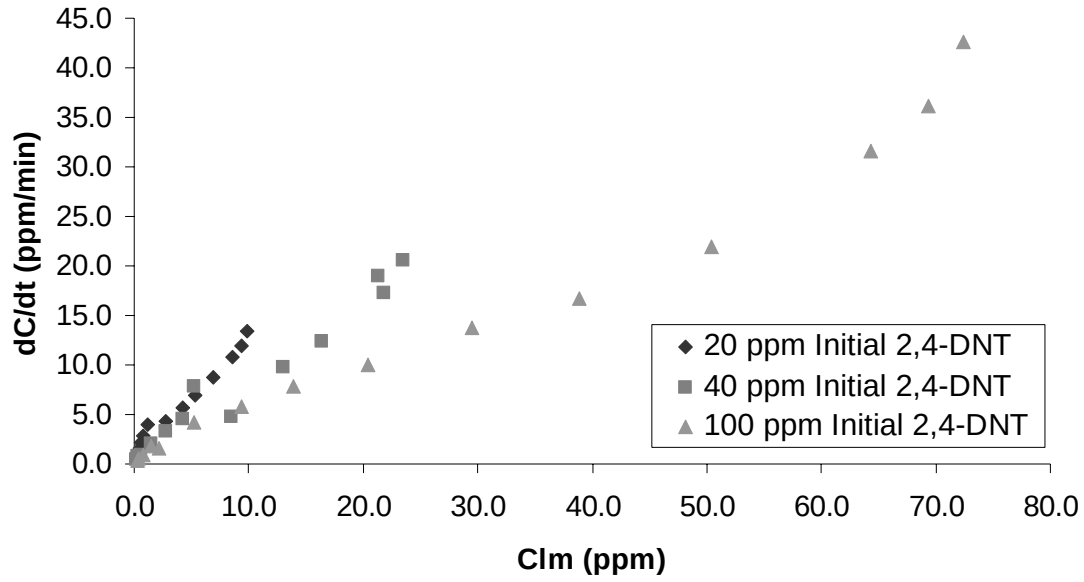

Figure 4.25 2,4-DNT degradation rate vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0

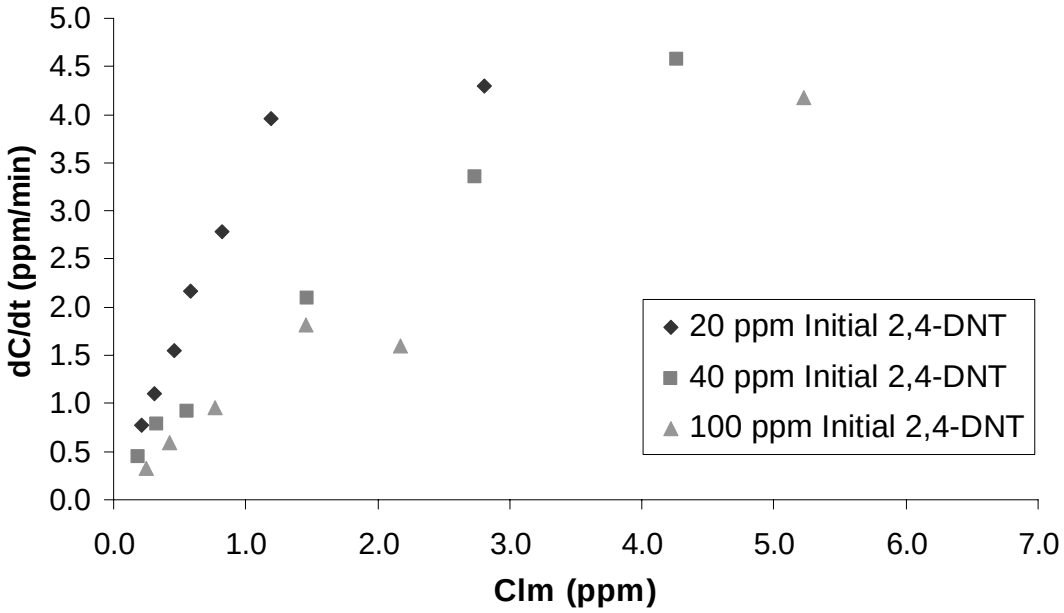

Figure 4.26 2,4-DNT degradation rate vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0 (zoom)

4.5.3 Effects of 2,4-DNT Initial Concentration on 2,4-DNT Byproducts.

Greater influent concentrations lead to greater concentrations of byproducts. Production of 2,4-DAT over time for three initial 2,4-DNT concentrations can be seen in Figure 4.27. The 2,4-DAT effluent concentration vs. C_{lm} graph shows that the amount of 2,4-DAT produced is similar for each concentration of initial 2,4-DNT. The amount of byproduct produced would indicate that system performance is the same, independent of initial 2,4-DNT concentration, which is contrary to evidence shown in Figure 4.25 above. The data observed from the unknown byproduct at 2.5 minutes (Unk 2.5) may account for the difference in the extent of reduction. At lower values of pH, there is a greater response for Unk 2.5 indicating greater concentrations of this unknown.

It appears that overall 2,4-DAT production is proportional to the initial influent 2,4-DNT concentration. The maximum concentration of 2,4-DAT seen in the 40 ppm experiment is almost double the concentration of 2,4-DAT produced in the 20 ppm experiment. In the 100 ppm experiment, the concentration of 2,4-DAT is much greater than the concentration seen in the 40 ppm experiment, though not more than double, as might be expected if there were no limitations of 2,4-DAT production.

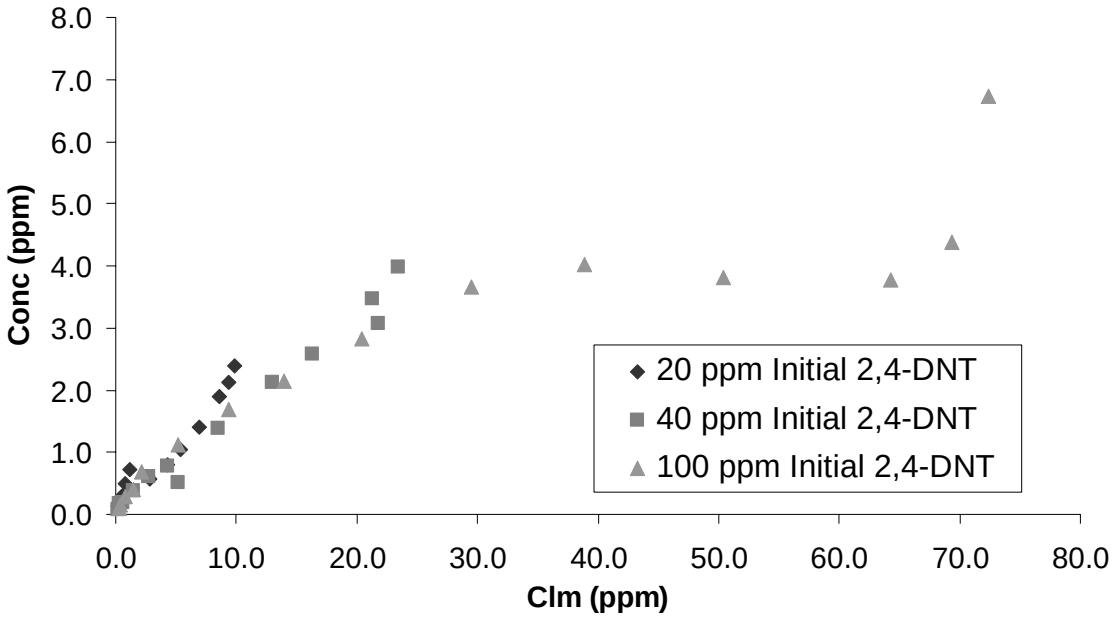

Figure 4.27 2,4-DAT effluent concentration vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0

The differences observed when comparing the intermediate 2A4NT and 4A2NT concentrations as a function of initial influent 2,4-DNT concentration are much more pronounced than what was observed for 2,4-DAT in Figure 4.27. At high initial influent 2,4-DNT concentrations, much higher concentrations of intermediates were observed (Figure 4.28 and 4.29). The concentration of 4A2NT produced was double the concentration of 2A4NT produced for each experiment. This may indicate that removal of the nitro group at the 4th carbon is the preferred reaction (producing 4A2NT). It is also possible the second reduction step to remove the nitro group at the 4th carbon (in 2A4NT) is faster than the removal of the nitro group at the 2nd carbon (in 4A2NT). This would mean the 2A4NT has a shorter half-life within the column. The greater amount of 4A2NT may also be caused by the extra step in reduction of 2,4-DNT described by Rajashekharam *et al*. (1997) (see Figure 2.6, Pathway 1). To produce 4A2NT the

reduction first goes through 4HA2NT. This causes the production of 4A2NT to occur later in the column and the 4A2NT may not have sufficient time remaining within the column to be reduced to 2,4-DAT.

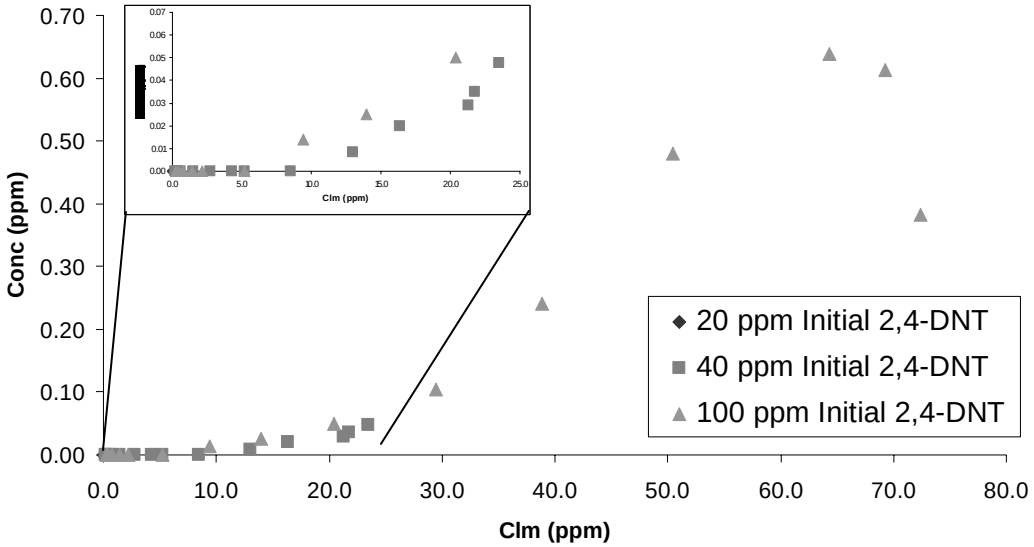

Figure 4.28 2A4NT effluent concentration vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0

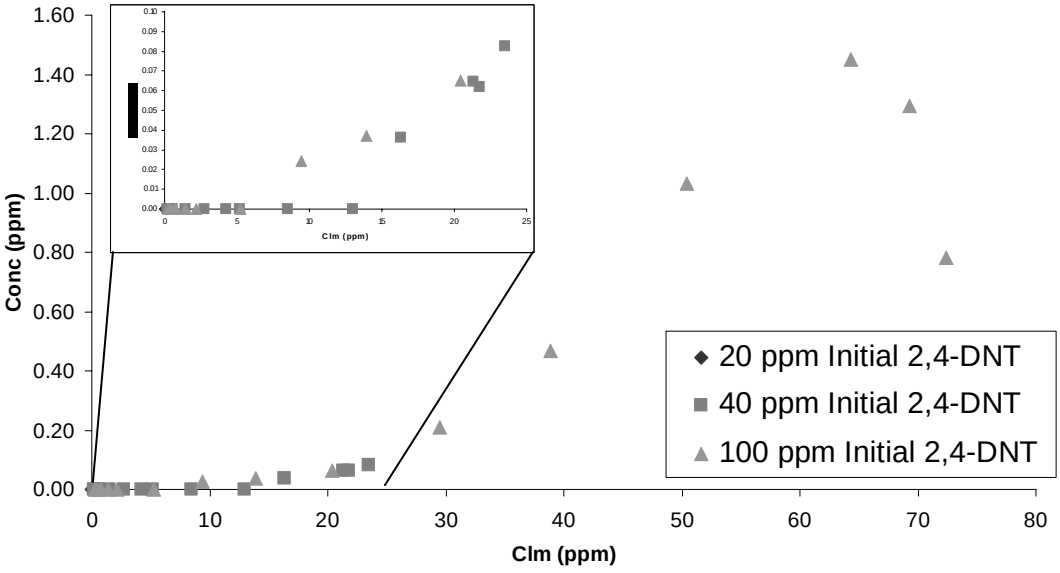

Figure 4.29 4A2NT effluent concentration vs. C_{lm} for differing initial concentrations of 2,4-DNT, 1 mMol formic acid, pH = 4.0

4.6 2A4NT Degradation

In an effort to gain insight into the intermediate reduction steps, Experiment #19 was conducted with 20 ppm of 2A4NT as the initial contaminant. The results can be seen in Appendix A. The 2A4NT was almost completely removed, with removal fractions ranging between 0.93 and 0.95 for the experiment. The Degradation Rate vs. C_{lm} graph showed linear behavior with $k_1 = 2.72\ min^{-1}$ (see Figure 4.30 below). The first sample point (highest C_{lm}) was not included in the regression as the effluent concentration of 2A4NT rose from the first sample point to the second sample point before falling. This can be attributed to non-steady state conditions within the column due to the excess formic acid at the beginning of the experiment.

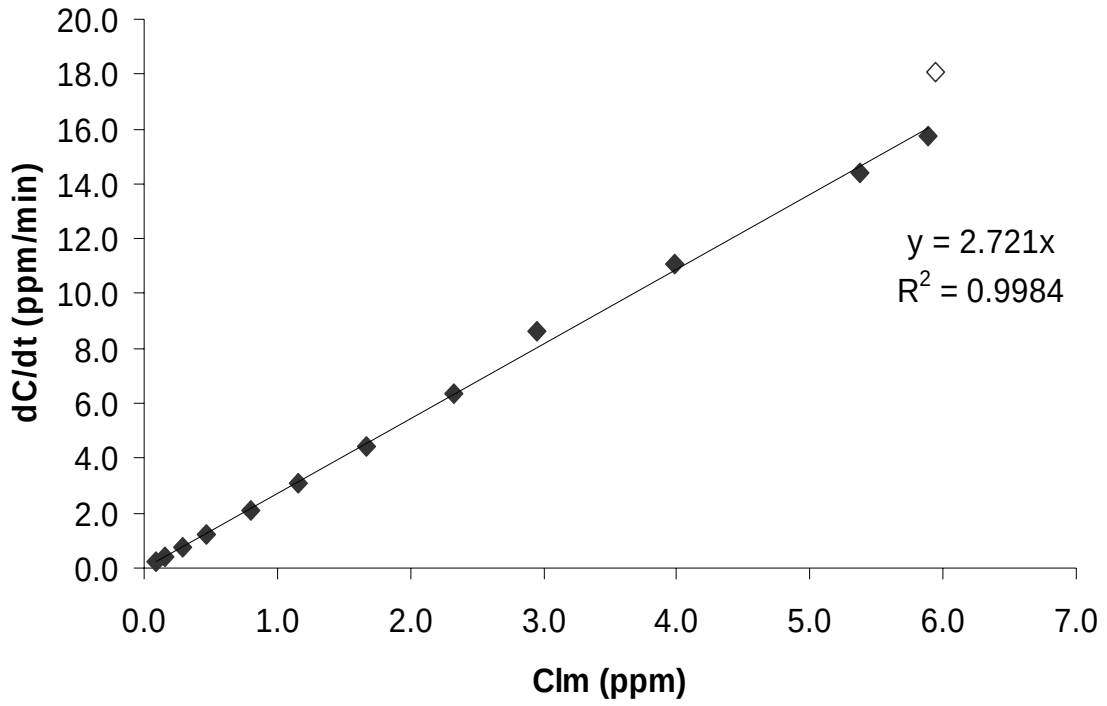

Figure 4.30 2A4NT degradation rate vs. C_{lm}, 20 ppm initial 2A4NT concentration, 4 mMol formic acid, pH = 4.0

The experiment produced a slightly greater amount of 2,4-DAT compared to Experiment #22 that had 20 ppm of 2,4-DNT as the initial contaminant. Experiment #19 produced 0.188 mMol of 2,4-DAT (31% of the influent) while Experiment #22 produced 0.128 mMol (25% of the influent). The high removal rates of 2A4NT support the observations from the 2,4-DNT experiments, where the concentrations of the intermediate 2A4NT were very low compared with the influent concentrations and the amount of 2,4-DAT produced. This indicates that the removal of the second nitro group is a fast reaction for 2A4NT, so it is a seen at only low concentrations in the effluent. Results from Experiment #23, where the initial concentration of 2,4-DNT was 100 ppm, show only 1.5 ppm of 4A2NT and 0.6 ppm of 2A4NT in the effluent, while 50 ppm of 2,4-DNT was removed. However, with almost complete removal of 2A4NT in Experiment #19, mass balance could account for only 45% of the mass. A majority of the mass could not be accounted for, indicating a number of unknown pathways that produce byproducts that are not visible at 254 nm with HPLC. One unidentified byproduct was visible on the HPLC and appeared with a residence time of 2.5 minutes, Unk 2.5. Unknown byproducts will be discussed in greater detail in Section 4.8.

4.7 Effects of Formic Acid on the Rate, Extent, and Byproducts of Pd-catalyzed 2,4-DAT Reduction

4.7.1 Effects of Formic Acid on Extent of 2,4-DAT Degradation.

A series of experiments (Experiment #8, #9,and #10) was conducted to examine the effect of formic acid on the reduction of 2,4-DAT and to determine if 2,4-DAT was

the final reduction product of 2,4-DNT or if it could be further transformed within the column. The possibility that 2,4-DAT was transformed to an unknown daughter product that cannot be detected with the current analytical method may explain the poor mass balance seen in all experiments. Experiments were conducted using 1, 4, and 0 mMol of formic acid. The experiment with no formic acid had a pH of 7.8 while the other two experiments were buffered to a pH of 4.0. Surprisingly, 2,4-DAT was removed even when no formic acid was present. The greater concentrations of formic acid led to greater removals (Figure 4.31), a trend seen before with the DNTs and seen by Phillips (2003) for the NTs. It is not clear what reduction reactions, if any, are taking place when no formic acid was present, or if the 2,4-DAT is being oxidized by residual oxygen in the water.

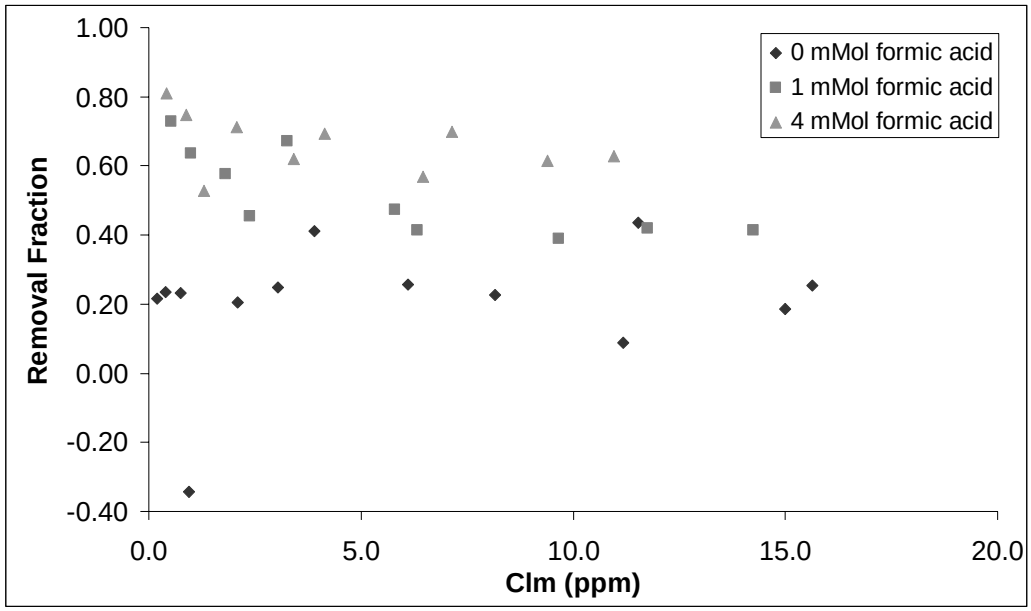

Figure 4.31 2,4-DAT removal fraction vs. C_{lm} for differing concentrations of formic acid, 20 ppm initial 2,4-DAT concentration, pH = 4.0

4.7.2 Effects of Formic Acid on 2,4-DAT Degradation Rates.

The effect of formic acid concentration on the degradation rates of 2,4-DAT was similar to the effects seen for 2,4-DNT, that is, higher concentrations of formic acid resulted in higher degradation rates (Figure 4.32). The data, as seen in Figure 4.32, are fairly erratic, either due to poor sampling and analytical procedures, poor mixing, inconsistent flow through the column, or some other unknown condition. Experiments conducted both before and after this series of experiments show smooth dilutions of the influent and effluent concentrations, but the data for this series of experiments (Experiments #8 - #10) are more variable, for an unknown reason. The influent curves for this series of experiments (Appendix A) also show erratic behavior, which may have been caused by poor mixing, sampling error, poor analysis, or another unknown factor.

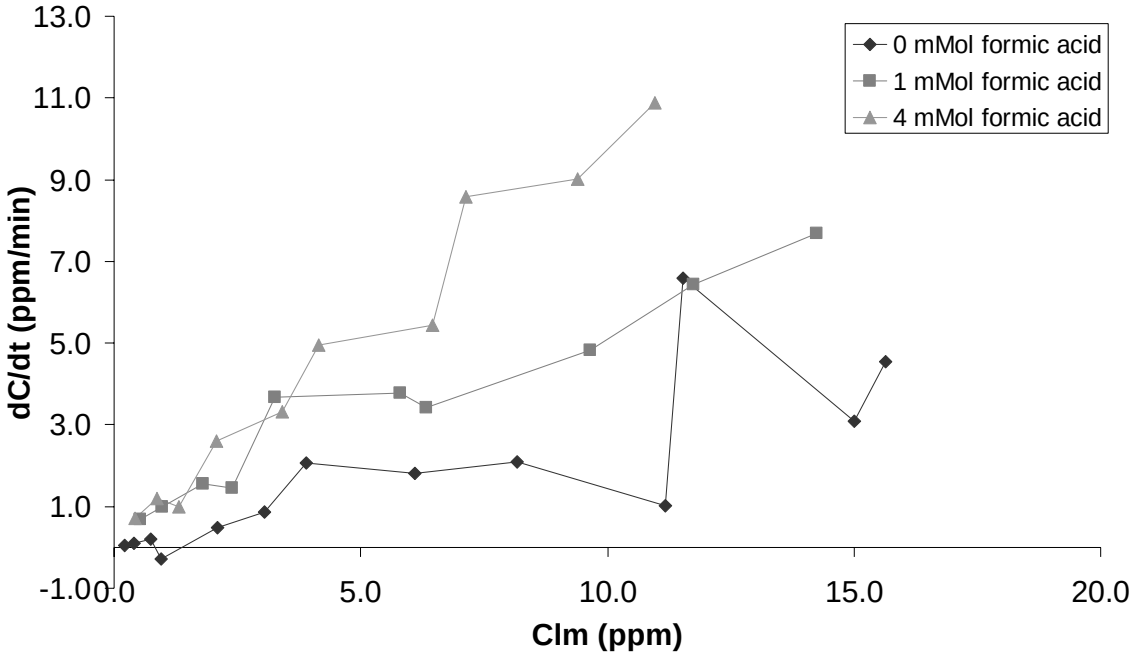

Figure 4.32 2,4-DAT degradation rate vs. C_{lm} for differing concentrations of formic acid, 20 ppm initial 2,4-DAT concentration, pH = 4.0

4.7.3 Effects of Formic Acid on 2,4-DAT Byproducts.

The reduction of 2,4-DAT did not produce any known byproducts. However, one unknown byproduct was seen during HPLC analysis with a residence time of 2.5 minutes. This byproduct was seen in both experiments with formic acid (see Appendix A). No byproducts were observed in the experiment with 0 mMol of formic acid, an indication that transformation was taking place without formic acid present, producing byproducts that could not be seen by the HPLC method used. When no formic acid was present, no byproducts were observed, although the removal fraction was consistently between 0.2 and 0.4 with only one outlier (see Appendix A). This is an indication that other transformation products not visible at 254 nm are being produced by some other mechanism. It is important to note that Experiment #11 was conducted to determine if 2,4-DNT behaved in a similar manner when no formic acid was present. It did not and no reduction of 2,4-DNT was seen, with only slight variations in influent and effluent concentrations that can be attributed to experimental variation. This is further evidence that the aminotoluenes are less persistent than the nitrotoluenes. A small number of samples from Experiment #13 were run through the HPLC and analyzed at 210 nm to determine if any cyclohexane was being produced; 210 nm being the maximum absorbance of cyclohexane. No cyclohexane was seen, and no other additional transformation products were observed at this wavelength.

The degradation of 2,4-DAT in the column does have implications regarding the overall mass balance for the 2,4-DNT experiments. Experiments #8 and #9 for 2,4-DAT had the same experimental conditions as Experiment #5 and #22 for 2,4-DNT. When the

degradation of the 2,4-DAT is considered when analyzing the 2,4-DNT reduction results, the mass balance improves. For example the average removal fraction of 2,4-DAT is 0.662 for Experiment #9. If the effluent concentrations of 2,4-DAT in Experiment #22 are all increased by C_{DAT}/(1-.662) the overall % Mass Identified improves as seen in Figure 4.33 below.

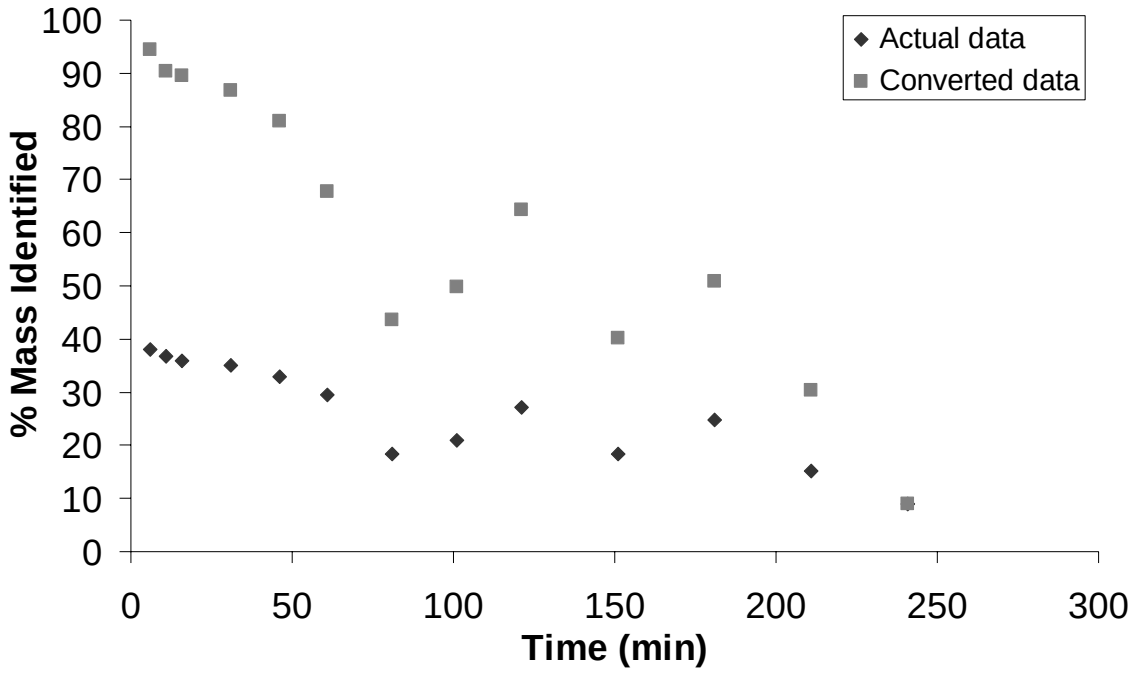

Figure 4.33 % mass identified vs. time for Experiment #22 with actual and converted 2,4-DAT mass data

4.8 Unknown Byproducts

Though the catalytic reduction produced the expected byproducts of 2A4NT, 4A2NT and 2,4-DAT (Rajashekharam *et al*., 1997; Neri *et al*., 1995) a number of other byproducts were seen during HPLC analysis. These other byproducts appeared to comprise a significant portion of the total amount of byproducts produced. With no

standards to compare to, it is not possible to determine the concentration of these unknown byproducts. The three unknown byproducts will each be discussed in detail below. Results from each experiment that produced these unknown byproducts can be seen in Appendix B. The unknown byproducts are labeled based on their residence time for the method of analysis as described in Section 3.4. The time reported is the elapsed time in minutes before the chemical created a measurable response in the detector. Figure 4.34 shows an HPLC response curve from Experiment #18 containing all of the known and unknown byproducts.

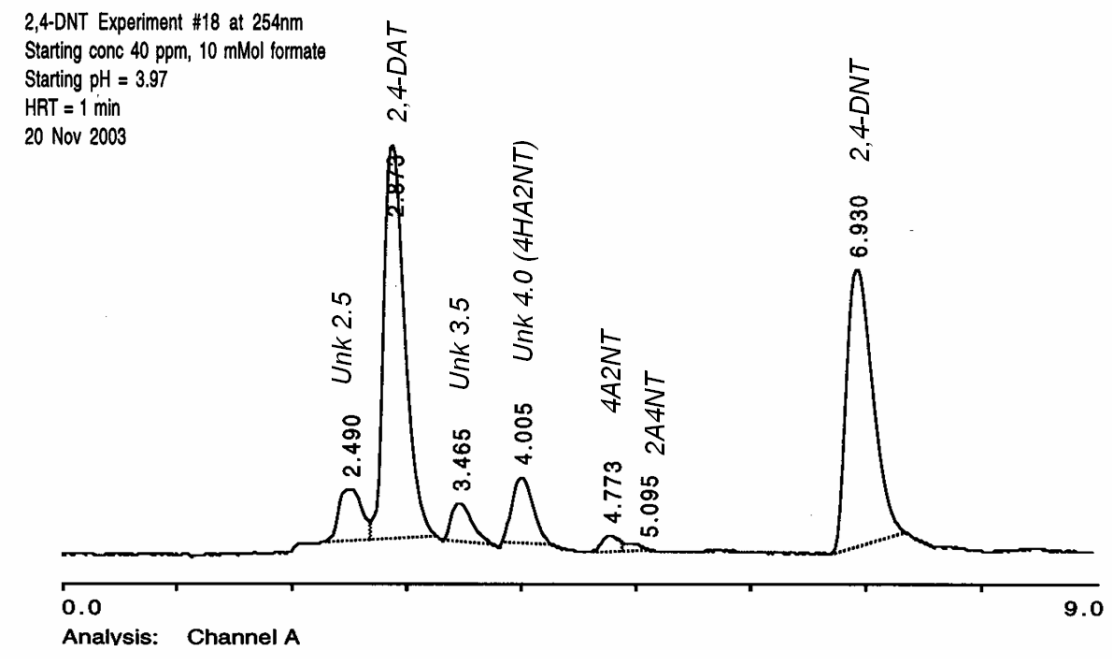

Figure 4.34 HPLC response curve from Experiment #18 showing all known and unknown byproducts

4.8.1 Unknown Byproduct at 2.5 Minutes HPLC Residence Time.

The first unknown byproduct appeared at 2.5 minutes (see Figure 4.34), labeled as Unk 2.5 in Appendix B. This was the first chemical to appear (2,4-DAT residence time

was 2.8 minutes) that was not attributed to minor responses that were also seen in the blank DI runs. Since the HPLC C18 column is a reversed-phased column, the stationary bed inside the column is nonpolar (hydrophobic), while the mobile phase is a polar (hydrophilic) liquid composed of a mixture of water and acetonitrile. This indicates that a polar compound will remain in the mobile phase and have a short retention time. The nonpolar material will sorb to the stationary phase and have longer retention times. The byproduct Unk 2.5 appears quickly, indicating it has a higher polarity compared to the other byproducts.

Unk 2.5 appears to be a byproduct of a reaction of 2,4-DAT inside the catalytic column. Experiments #8, #9, and #10 were conducted to examine the behavior of 2,4-DAT in the system (see Section 4.7). In Experiments #8 and #9, Unk 2.5 was visible and its response in the HPLC composed about 8% of the area of the entire HPLC response curve. Unk 2.5 appears in a significant number of other experiments, but its appearance in Experiments #8 and #9 indicate it is a product of 2,4-DAT transformation.

When the formic acid concentration is only 1 mMol and the influent concentration of 2,4-DNT is only 20 ppm, Unk 2.5 does not appear in the effluent. For experiments conducted with 4 and 10 mMol formic acid, Unk 2.5 does appear. At lower values of pH the HPLC response for Unk 2.5 is greater (see Figure 4.35). Also, higher concentrations of formic acid lead to greater HPLC response for this byproduct as seen in Appendix B. Though the actual concentration may not be determined, we may speculate that this byproduct does not have a significant effect on the total mass balance. The known contaminant concentrations are found by running standards and plotting the HPLC response area versus the known standard concentration (see Appendix C for standards).

The slope of the line gives the conversion value to change a known HPLC response into a concentration. The known contaminant standards all have slope values within one order of magnitude. All are 10^{-5} for the conversion of HPLC response to concentration (ppm). Using a value of $1x10^{-4}$, which would greatly overestimate the concentration of the known NACs, for conversion and the maximum HPLC response for Unk 2.5 from all experiments (HPLC Response = 19,518 from Exp #20) the maximum concentration would be 1.952 ppm. Though this would be a significant fraction of the byproducts produced, it would have only a minor effect on the total mass balance. When the influent 2,4-DNT concentration was 100 ppm, a smaller response at 2.5 minutes occurred for pH = 4.0 and no response was seen when pH = 5.05. The data suggest that with only 1 mMol of formic acid, the pH must be near 4.0 to produce this byproduct. At a pH of 5, even starting with a 2,4-DNT concentration of 100 ppm, Unk 2.5 was not observed.

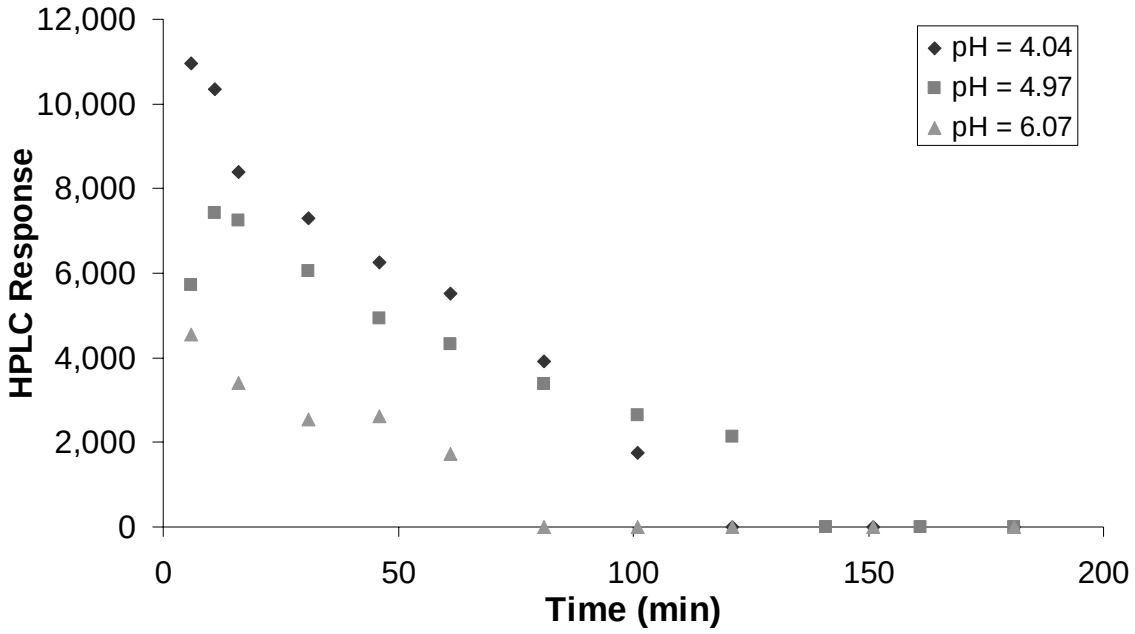

Figure 4.35 Unk 2.5 HPLC response vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 10 mMol formic acid

4.8.2 Unknown Byproduct at 3.4 Minutes HPLC Residence Time.

The second unknown byproduct, Unk 3.4, appeared just after the 2,4-DAT (see Figure 4.34) indicating a slightly less polar compound when compared to 2,4-DAT. This byproduct also was not in evidence in experiments with 1 mMol formic acid and starting concentrations of 20 ppm 2,4-DNT. The appearance of Unk 3.4 was not consistent and its response in the HPLC was generally less than that for Unk 2.5. For a number of experiments, the response associated with Unk 3.4 was greater at increased values of pH, a trend not seen for other byproducts, though for other experiments lower values of pH produced more response. The response for Unk 3.4 was greater at higher concentrations of formic acid.

The response of Unk 3.4 appears to have greater dependence on the initial influent 2,4-DNT concentration than on other parameters. The maximum responses at initial influent concentrations of 20 ppm were around 4,000 while at 40 ppm responses were as high as 14,400. The greatest HPLC response was seen for the two experiments with 100 ppm initial influent concentrations; a maximum response of 77,884 for pH = 4.0 and 50,049 for pH = 5.05. Using the same approach as was used in Section 4.8.1 for Unk 2.5, it can be estimated that the maximum concentration of Unk 3.4 would be about 8 ppm (observed in Experiment #23). This would be a significant fraction of the byproducts generated (the corresponding concentration of 2,4-DAT in Experiment #23 was 3.78 ppm). It would also have a significant, though presently unquantifiable, effect on the overall mass balance.

4.8.3 Unknown Byproduct at 4.0 Minutes HPLC Residence Time.

The last unknown byproduct, Unk 4.0, appears between 2,4-DAT and the two amino-nitro intermediates, 2A4NT and 4A2NT. This byproduct also was not observed for experiments with 1 mMol formic acid and initial concentrations of 20 ppm 2,4-DNT. At 4 mMol formic acid, the pH had an effect with the most Unk 4.0 appearing at pH = 5.05, then 6.0, and the least at pH = 4.0. When the formic acid concentration was raised to 10 mMol the pH did not greatly affect the Unk 4.0 that was observed and HPLC responses were similar with slightly more appearing at pH = 4.97 (Figure 4.36).

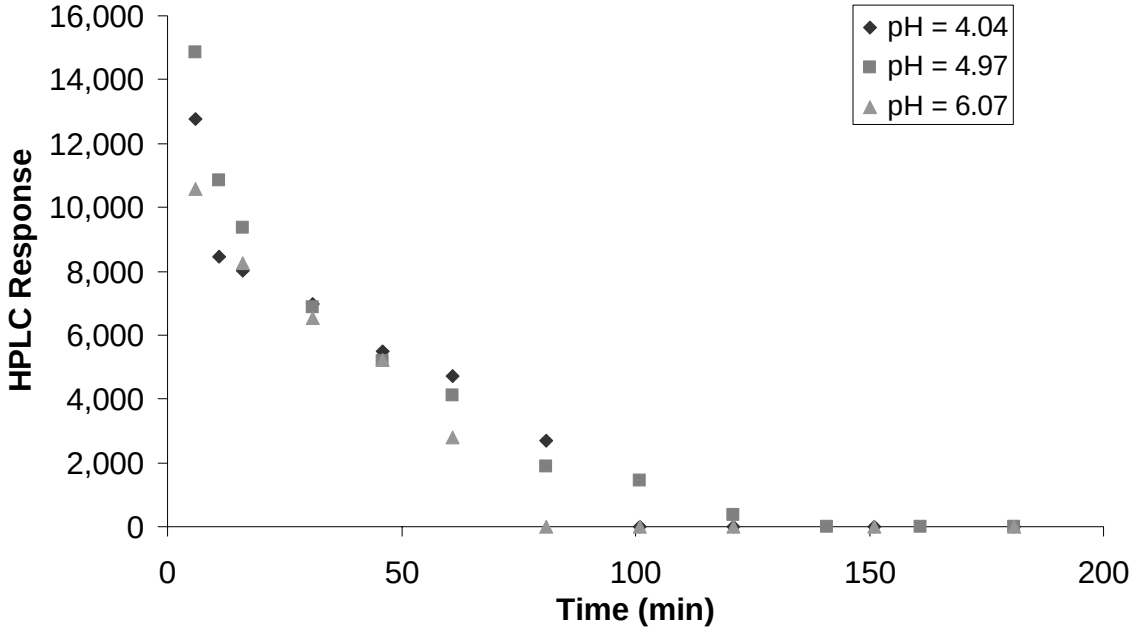

Figure 4.36 Unk 4.0 HPLC response vs. time for differing values of pH, 20 ppm initial 2,4-DNT concentration, 10 mMol formic acid

For almost all 2,4-DNT experiments, the higher concentrations of formic acid produced greater amounts of Unk 4.0. The formation of Unk 4.0 appears to be influenced more by the concentration of formic acid than the pH. For pH values of 4.04, 4.97, and 6.07 at 10 mMol formic acid, the Unk 4.0 maximum response was 12,779; 14,846; and

10,574 respectively. With the influent 2,4-DNT concentration at 100 ppm, only the first two samples showed Unk 4.0 for pH = 4.0 and no samples showed Unk 4.0 when pH = 5.0. Since both experiments were conducted with 1 mMol formic acid, this agrees with data gathered from the earlier series of experiments conducted at 1 mMol formic acid.

Studies conducted by Rajashekharam *et al*. (1997) and Neri *et al*. (1995) support the possibility that Unk 4.0 is actually 4-hydroxylamine, 2-nitrotoluene (4HA2NT). Both researchers show 4HA2NT as a possible intermediate in the 2,4-DNT reduction pathway. Neri *et al*. (1995) presented an HPLC output, Figure 4.37, which shows 4HA2NT appears almost exactly between 2,4-DAT and 2A4NT, the same location Unk 4.0 appears. The 4HA2NT is an unstable transient byproduct that spontaneously degrades in a matter of hours, with almost complete disappearance after one day (Neri *et al*., 1995). Sampling for the 2,4-DNT experiments was done within 4 hours so it is highly probable that 4HA2NT would still be present in the samples if it was initially formed during the reduction process.

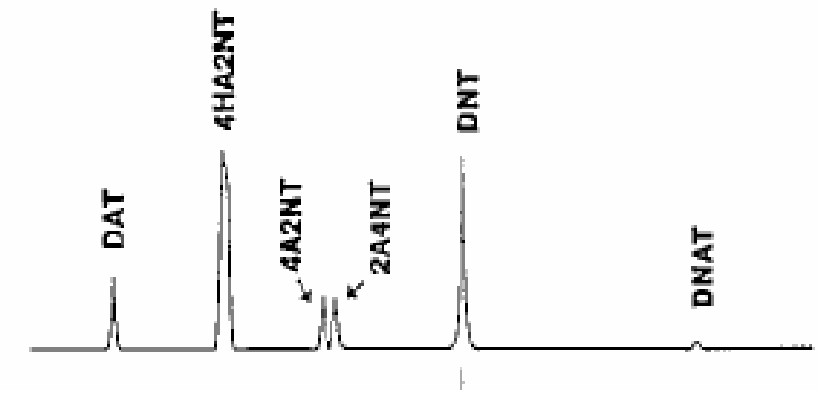

Figure 4.37 HPLC Analysis of 2,4-DNT reduction (Neri *et al*., 1995)

4.9 Potential for In Situ Remediation

As will be discussed below, based on the kinetic parameters, palladium catalyzed degradation of 2,4-DNT would be possible in an *in situ* recirculation well application. The known byproducts have some health effects (see Section 2.4) but are less toxic and less persistent than the parent NAC contaminant. Further research must be conducted to determine the identification of the unknown byproducts before overall health risks can be assessed.

Assuming upgradient 2,4-DNT concentrations of 20 ppm, 4 mMol formic acid could be added, which would result in a first-order reaction rate constant (based on Experiment #9) of $k_1 = 1.0\ min^{-1}$. Based on calculations with this rate constant, an in-well reactor would require a residence time of approximately 4.56 minutes for 99% 2,4-DNT destruction. By increasing the formic acid concentration to 10 mMol and using a first-order rate constant based on Experiment #15 of $3.19\ min^{-1}$ the residence time would drop to 1.45 minutes; a time very close to the residence time reported by Phillips (2003) for a hypothetical in-well system.

Experiment Number	Contaminant	pH	Formic Acid (mMol)	Initial Conc (ppm)	Kinetic Parameters (min^{-1})
3	2-NT	5.15	1	20	$k_1 = 0.4103$ $R^2 = .9941$
6	2,4-DNT	5.00	1	20	$k_1 = 0.6354$ $R^2 = .995$
9	2,4-DAT	3.96	4	20	$k_1 = 1.0098$ $R^2 = .9743$
12	2,4-DNT	4.00	4	15	$k_1 = 3.4513$ $R^2 = .9857$
15	2,4-DNT	4.04	10	20	$k_1 = 3.1867$ $R^2 = .9959$
16	2,4-DNT	4.97	10	20	$k_1 = 2.4426$ $R^2 = .9989$
17	2,4-DNT	6.06	10	20	$k_1 = 2.0985$ $R^2 = .9994$
18	2,4-DNT	3.97	10	40	$k_1 = 2.8208$ $R^2 = .9989$
19	2A4NT	4.00	4	20	$k_1 = 2.7205$ $R^2 = .9984$
22	2,4-DNT	4.00	4	20	$k_1 = 2.4831$ $R^2 = .9979$

Table 4.2 Column experiments (results exhibit first-order kinetic behavior)

5.0 CONCLUSIONS

5.1 Summary

In this thesis the use of a palladium catalyst with formic acid as an electron donor to remediate a nitroaromatic contaminant was investigated. A flow through column experiment was designed to study reaction rate, extent, and byproduct formation, by the reduction of 2,4-dinitrotoluene (2,4-DNT). Reduction of the intermediate byproduct 2A4NT and final product 2,4-DAT was also examined to gain a further understanding of the system. The effect of three different parameters on system performance was evaluated in the course of experimentation for 2,4-DNT: initial pH, formic acid concentration, and contaminant concentration. Results were modeled using first-order and Michaelis-Menten kinetics.

The complete pathway for reduction was not determined due to the presence of unknown byproducts observed during 2,4-DNT reduction. It is not known if these byproducts indicate additional reduction pathways or are transformations due to direct reactions with formic acid or the palladium catalyst. These additional byproducts were not reported in earlier work with palladium while hydrogen gas was the electron donor. Should similar unknown byproducts appear with TNT reduction, it may indicate new pathways exist that do not lead to TAT as a final reduction product.

5.2 Conclusions

Nitrotoluenes are reduced to their corresponding aminotoluenes. Experimental results show that the mononitrotoluene 2-NT is reduced by a Pd-catalyzed system to 2-aminotoluene when formic acid is used as an electron donor. This was the only byproduct observed in the column effluent. However, lack of mass balance indicates that other undetected byproducts or transformation products may also be present in the effluent.

Extent and rate of 2,4-DNT degradation is dependent on the influent pH. At lower values of pH, greater degradation was seen. Lower values of pH produce more favorable reducing conditions due to the greater presence of free hydrogen. The lower pH also reduced the concentration of hydroxide ions that bind to palladium sites and deactivate the catalyst. Though the pH is of great importance in the system, limitations due to a higher pH can be overcome by higher concentrations of formic acid.

Extent and rate of 2,4-DNT degradation is highly dependent on the concentration of formic acid. The formic acid is used as an electron donor to drive the reaction. Without an electron donor the reduction reaction does not occur in the palladium system, regardless of the pH. Experimental results show that with no formic acid, there is no degradation of 2,4-DNT. The greater concentrations of formic acid led to increased amounts of degradation in the column experiments. However, at low values of pH less formic acid is necessary to obtain similar reaction rates. The lower amount of hydroxide ion at low pH compensates for a lower concentration of formic acid.

Extent and rate of 2,4-DNT degradation is dependent on the initial concentration of the contaminant. The higher initial concentrations of contaminant led to lower degradation rates at similar values of C_{lm}. However, the system still performed even at initial concentrations as high as 100 ppm, with approximately 40% removal, increasing to 75% as the 2,4-DNT concentrations dropped below 20 ppm. This is significantly lower than removals observed when initial concentrations were only 20 ppm (75%, increasing to 97%). The ability for the palladium system to degrade high concentrations of 2,4-DNT, even at a reduced extent, shows it is a viable option for areas of high contaminant concentrations where other methods may not be applicable.

Intermediate reduction steps are not rate limiting. The intermediate reduction products do not limit the overall reduction reaction of 2,4-DNT. Experiments show that concentrations of these intermediates are quite low compared to influent concentrations and reduction end products. Experiment #19 which used 20 ppm of 2A4NT as the initial contaminant showed that greater than 92% of 2A4NT was removed throughout the entire experiment. The high removal rate and low concentration of these intermediates suggest they are quickly reduced within the system.

2,4-DNT degradation produces expected and unexpected byproducts. The expected intermediates of 2A4NT, 4A2NT, and 2,4-DAT were observed as byproducts of the reduction reaction. However, three other byproducts were observed that were not identified. One is believed to be 4HA2NT as seen in previous research. Another appears to be a result of 2,4-DAT reduction or is a hydrogenated form of 2,4-DAT. The other is unknown, and no speculation may be made at this time.

More complex NACs such as TNT, HMX, and RDX may be reduced by Pd-catalysis. The research conducted by Phillips (2003) and results obtained from this effort show a distinct possibility for Pd-catalyzed reduction of more complex nitroaromatics. Research has shown that TNT can be reduced to triaminotoluene (TAT) (Hwang *et al*., 1998). Based on the current study of NT and DNT reduction, which resulted in the production of the corresponding aminotoluenes, it is hypothesized that reduction of TNT to TAT will probably occur with a Pd-catalyzed system using formic acid as the electron donor. As the reduction occurs at the nitro functional group, other complex NACs such as HMX and RDX may also be reduced with this system.

5.3 Future Work

Study behavior of intermediates. The reduction and byproducts of the aminonitrotoluenes should be examined to gain an understanding of the fate of these chemicals. This research can then be applied to reduction of 2,4-DNT in an effort to better quantify and identify byproducts and reaction schemes.

Extend Studies to other NACs. This thesis examined the reduction of 2,4-DNT, one of the simplest nitroaromatic compounds. Future work should examine the susceptibility of the isomers of DNT and other compounds such as TNT, RDX, and HMX to Pd-catalyzed reduction.

Characterize unknown byproducts. The reduction of 2,4-DNT using a palladium catalyst and formic acid as an electron donor resulted in a number of unidentified byproducts. The HPLC employed was not able to identify these unknown byproducts.

Use of a GCMS may lead to positive identification and a greater understanding of the reduction reactions.

Continued investigation and optimization of 2,4-DNT reduction using Pd-catalysis with formic acid as a reductant. This thesis only examined the effect of three parameters on system performance, over a limited range of conditions. The range of experiments may be expanded or additional parameters, such as competing dissolved ions or contaminant mixtures, studied. Continued research will allow for optimization of the system, improving overall performance and defining operating parameters for possible future field applications.

Use kinetic data to model a recirculation well system. Models of catalytic reactors as components of recirculation well systems have been applied to other contaminants, to determine the feasibility of field application. Kinetic data from this work and from Phillips (2003) may be incorporated into a recirculating well model to determine the feasibility of field application of Pd-catalysis to effect *in situ* degradation of NACs.

Study health effects of NAC reduction byproducts. The health effects and overall toxicity of NAC reduction products, both known and unknown, should be studied. Should the byproducts of palladium-catalyzed reduction of NACs pose health risks, this process may not be useful for groundwater remediation.

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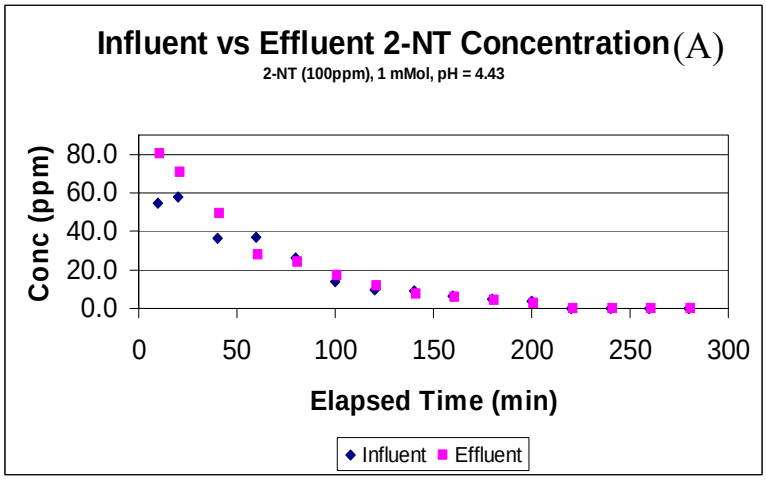
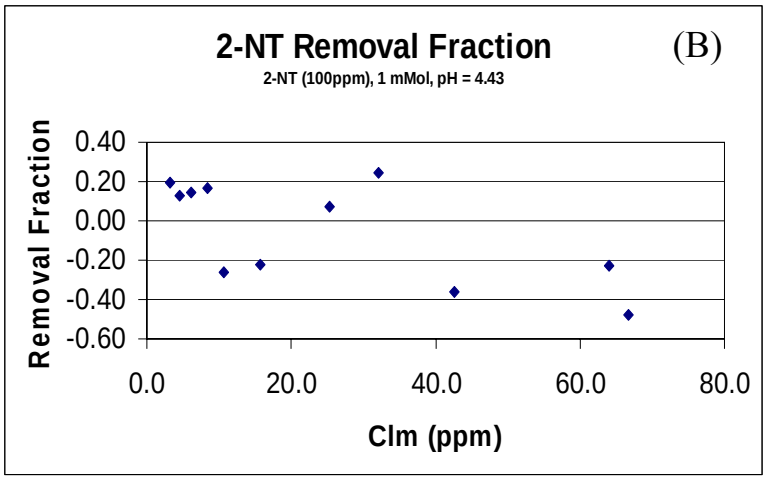
VITA

Captain Mark R. Stevens was born in San Antonio, TX. He graduated from Bellevue East High School in 1995 and received an appointment to the United States Air Force Academy. At the Air Force Academy he received a Bachelors of Science degree in Environmental Engineering and a commission in the United States Air Force on 2 June 1999. In August 2003 he matriculated into the Graduate Engineering Management program at the Air Force Institute of Technology.

APPENDIX A

COLUMN EXPERIMENT RESULTS





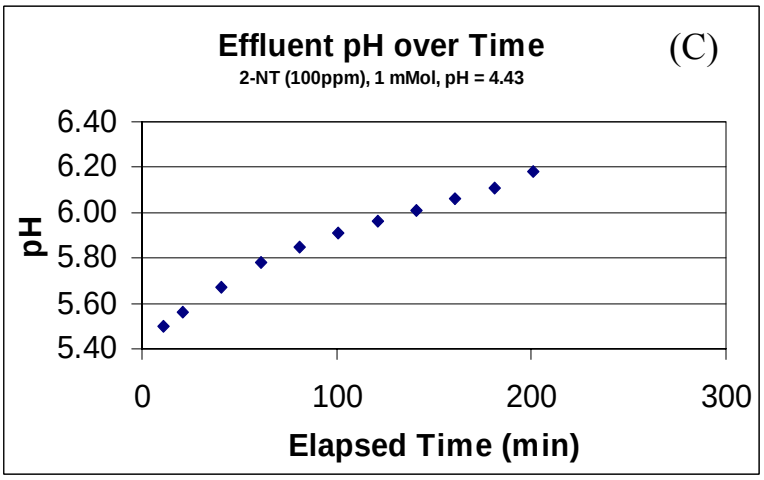
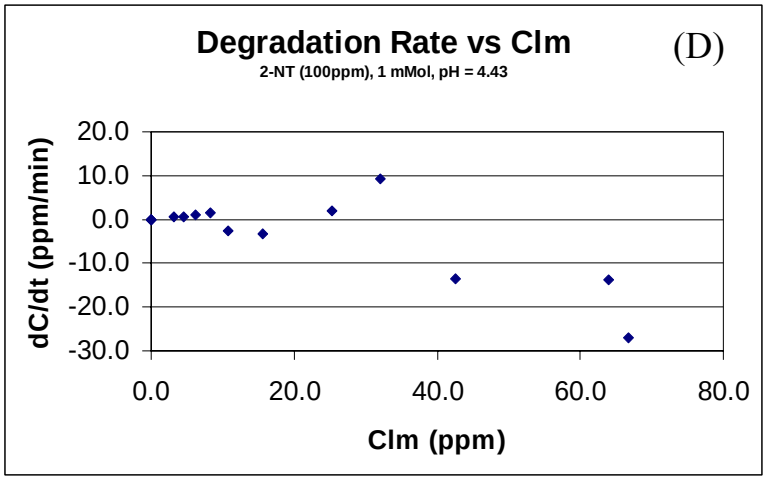
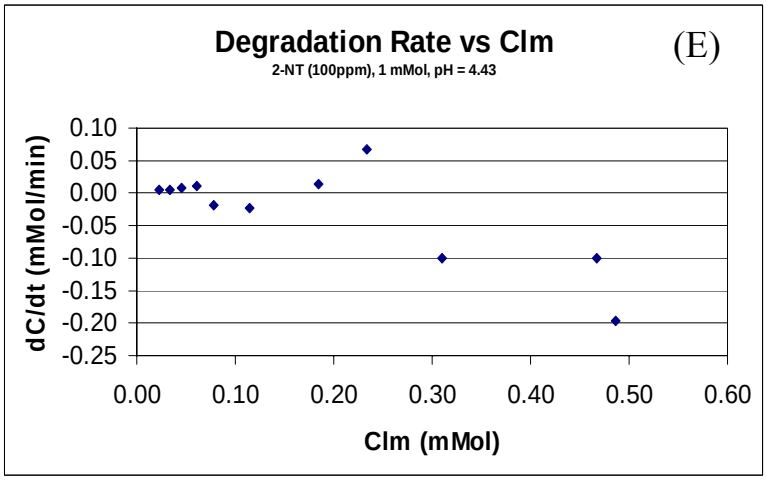


Figure A.1a Exp #1 – 100 ppm 2-NT, 1mMol Formic acid, pH = 4.43 (A) Influent vs. Effluent 2-NT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time





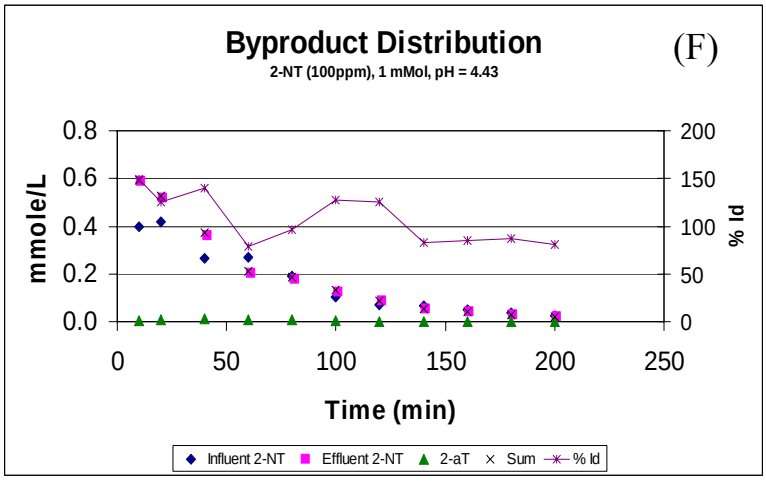
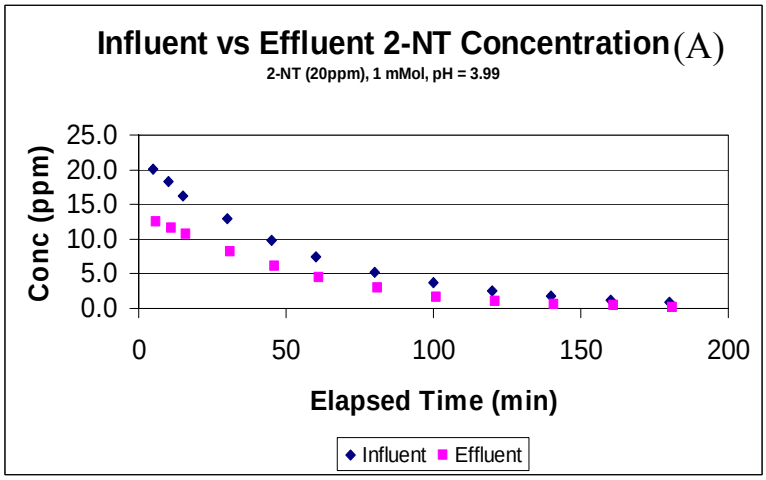
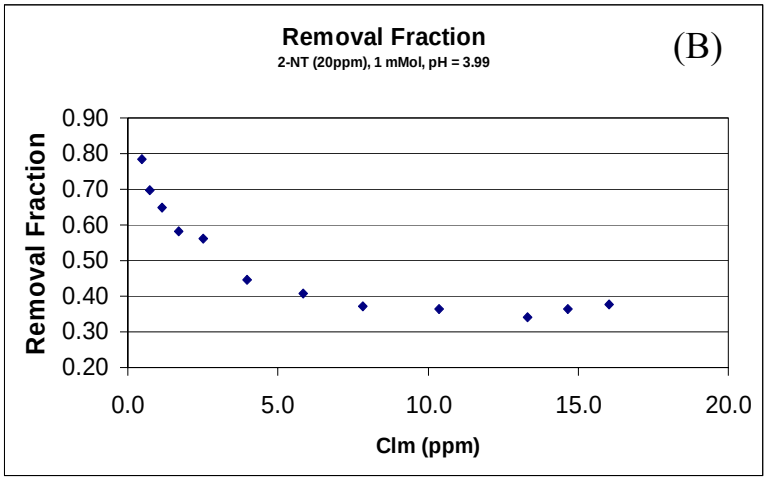


Figure A.1b Exp #1 – 100 ppm 2-NT, 1mMol Formic acid, pH = 4.43 (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol) (F) Byproduct Distribution





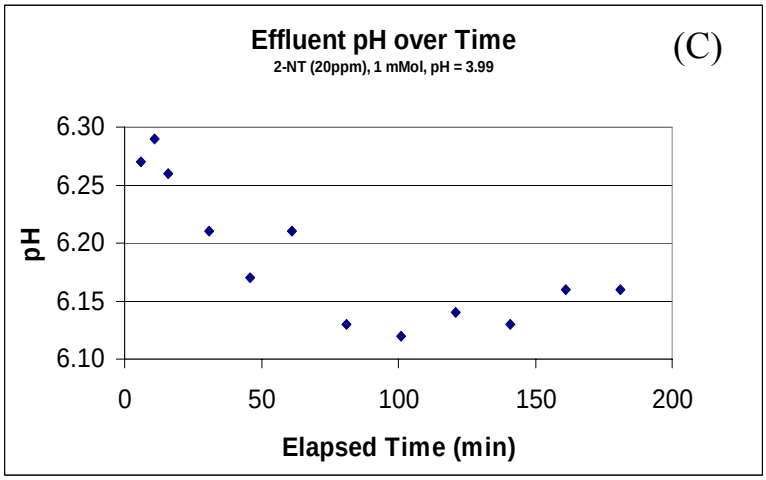


Figure A.2a Exp #2 – 20 ppm 2-NT, 1mMol Formic acid, pH = 3.99 (A) Influent vs. Effluent 2-NT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time

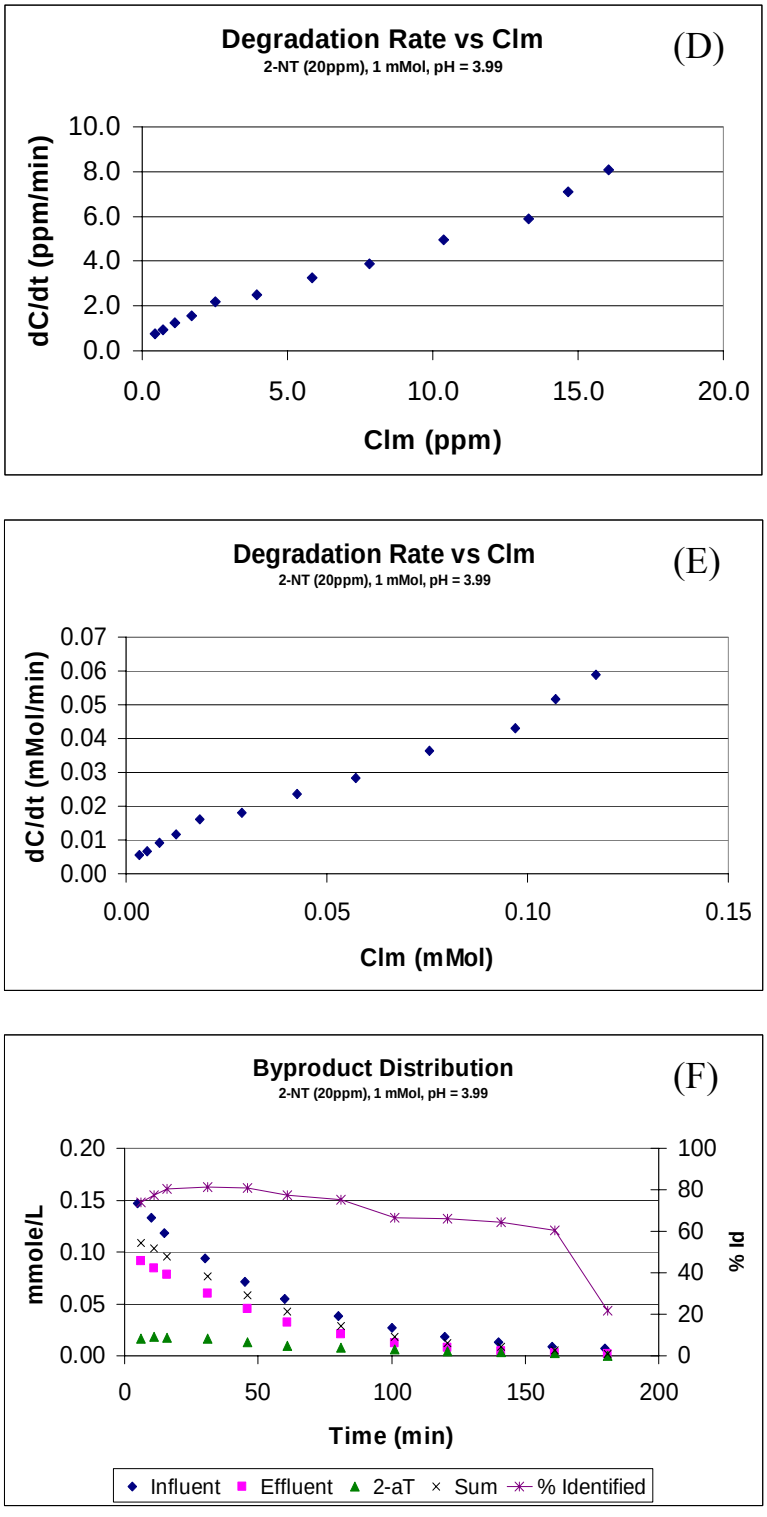
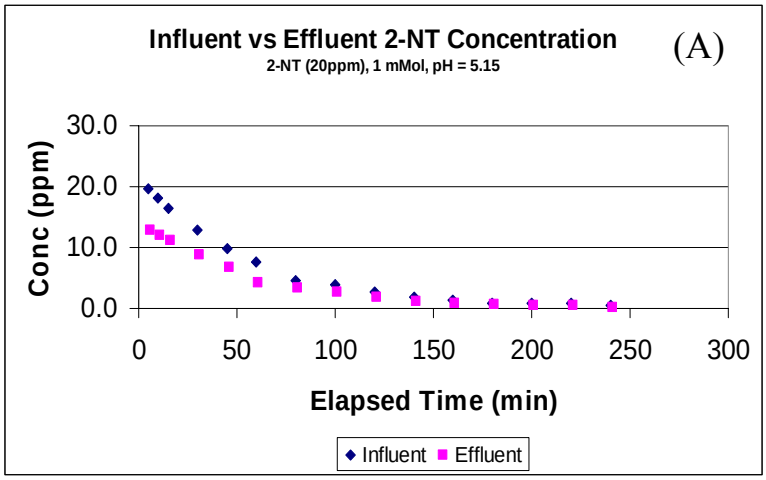
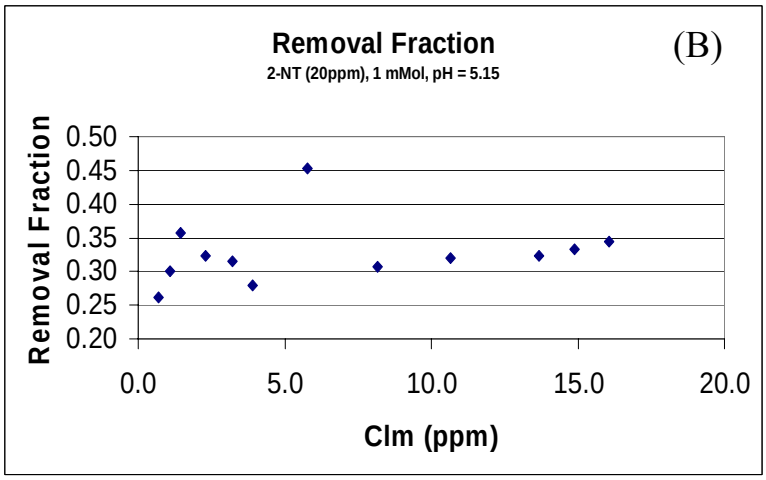


Figure A.2b Exp #2 – 20 ppm 2-NT, 1mMol Formic acid, pH = 3.99 (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol) (F) Byproduct Distribution





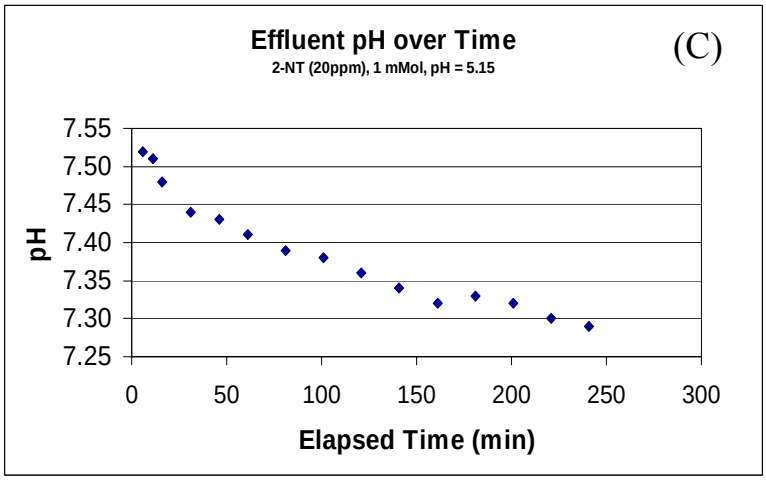


Figure A.3a Exp #3 – 20 ppm 2-NT, 1mMol Formic acid, pH = 5.15 (A) Influent vs. Effluent 2-NT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time

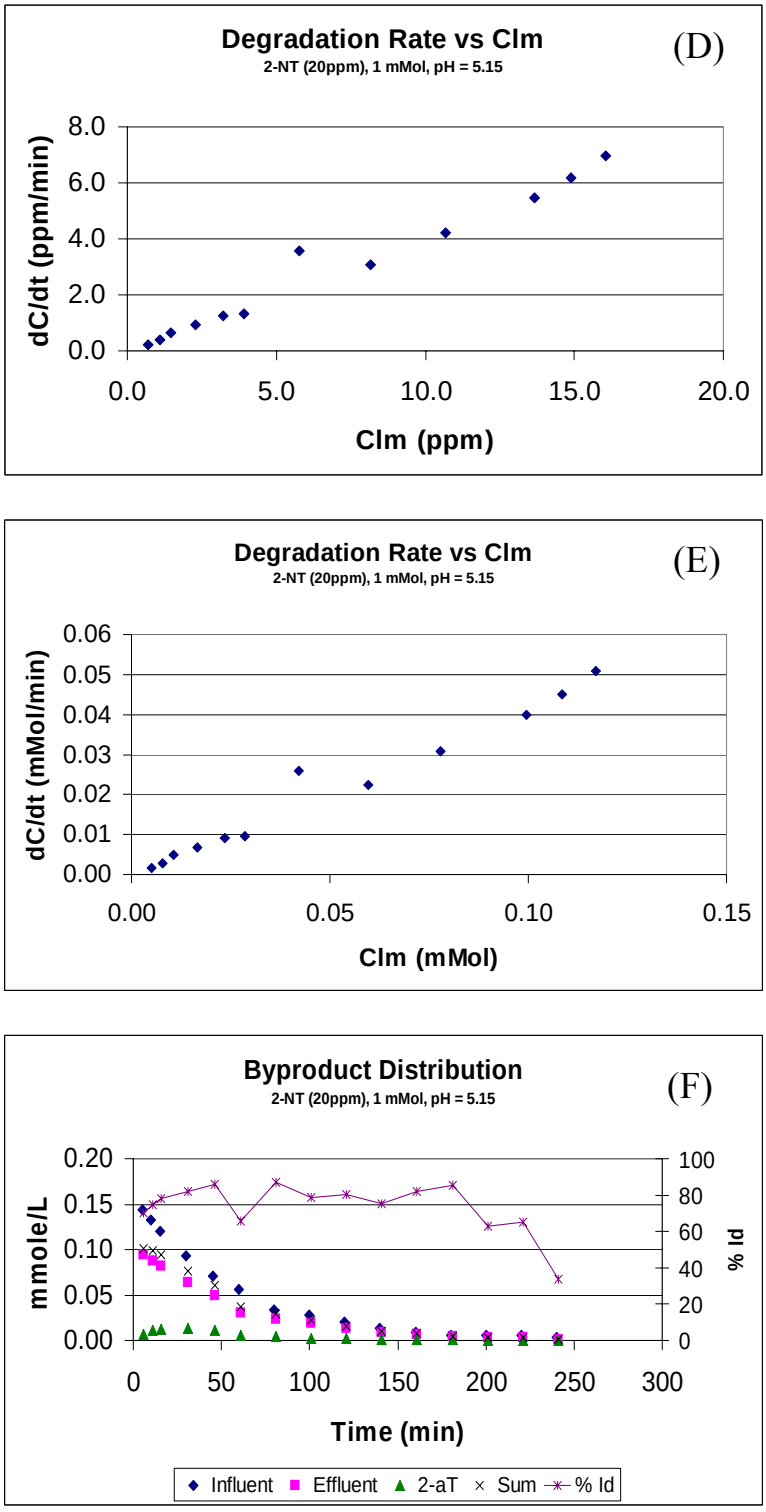


Figure A.3b Exp #3 – 20 ppm 2-NT, 1mMol Formic acid, pH = 5.15 (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol) (F) Byproduct Distribution

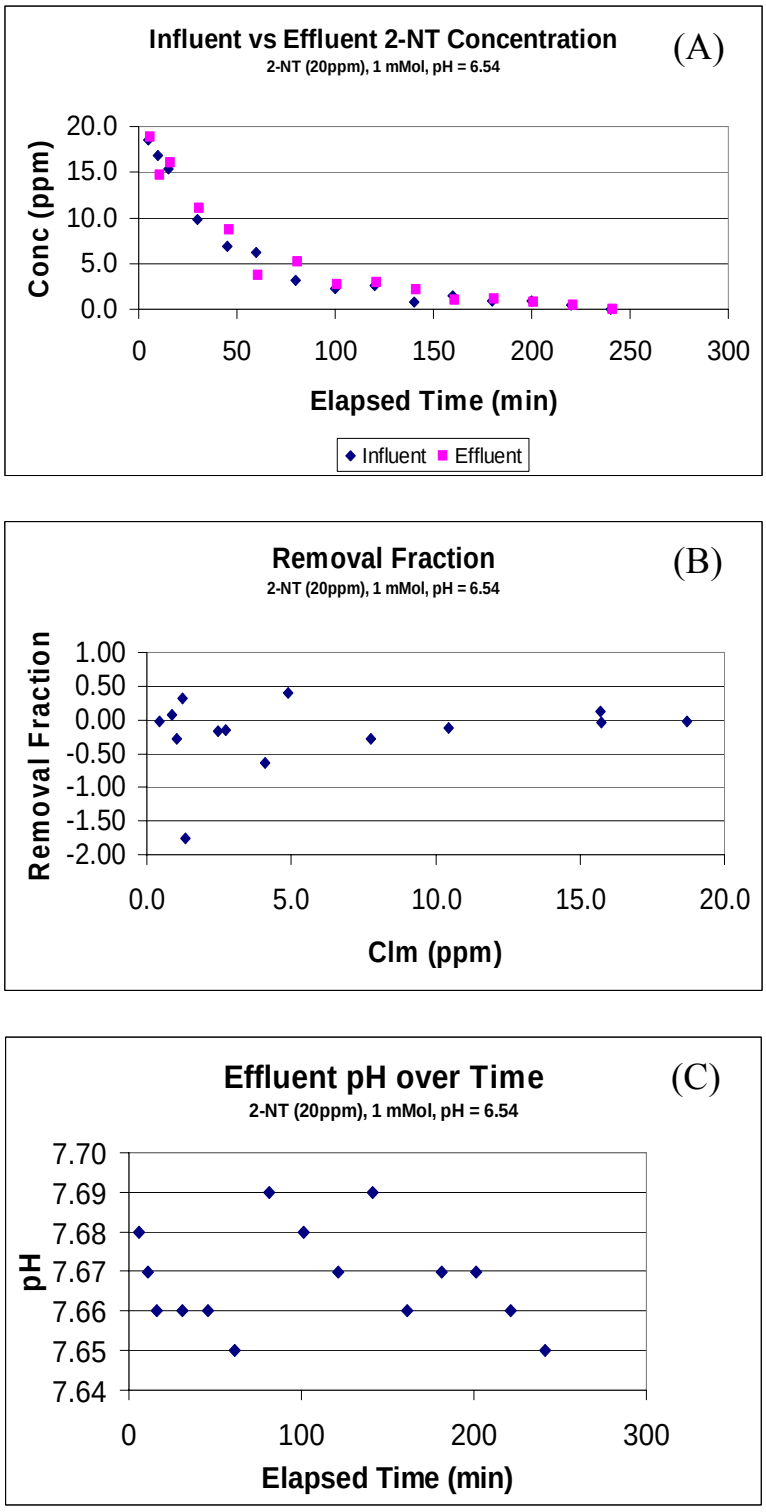
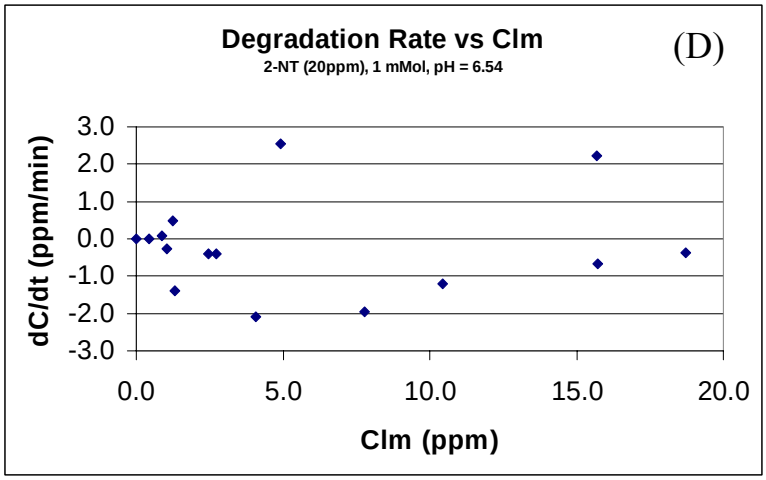
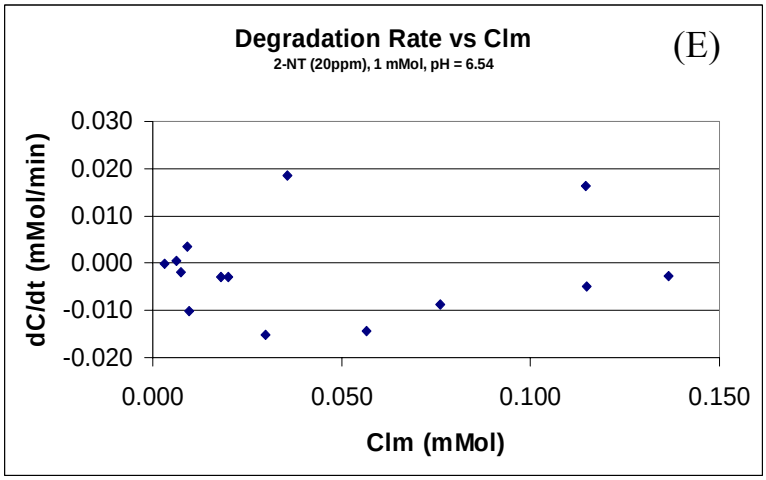


Figure A.4a Exp #4 – 20 ppm 2-NT, 1mMol Formic acid, pH = 6.54 (A) Influent vs. Effluent 2-NT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time





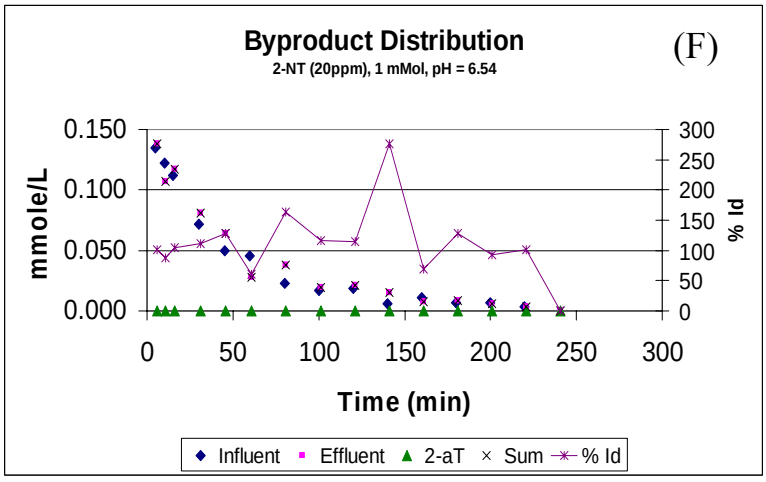


Figure A.4b Exp #4 – 20 ppm 2-NT, 1mMol Formic acid, pH = 6.54 (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol) (F) Byproduct Distribution

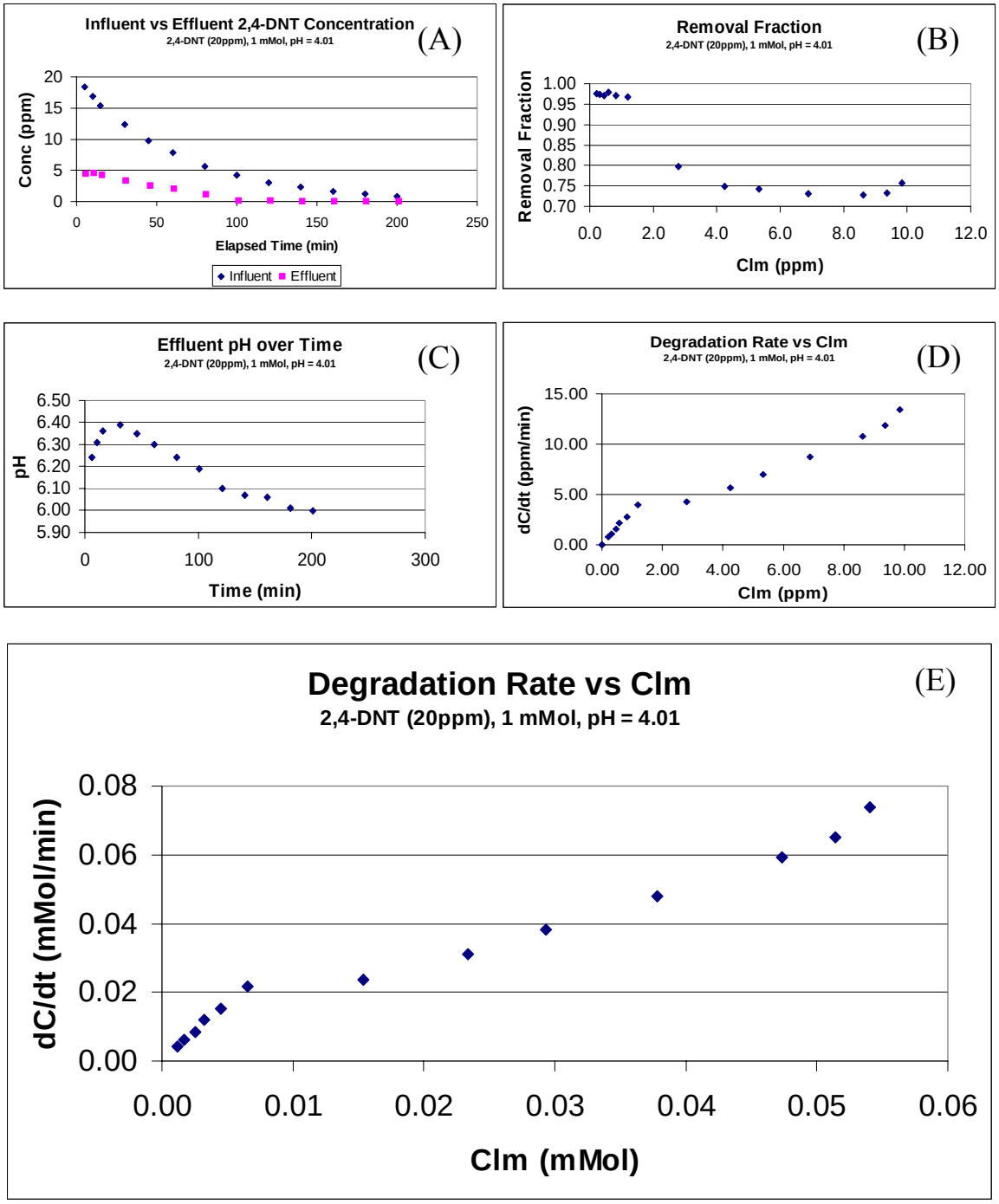
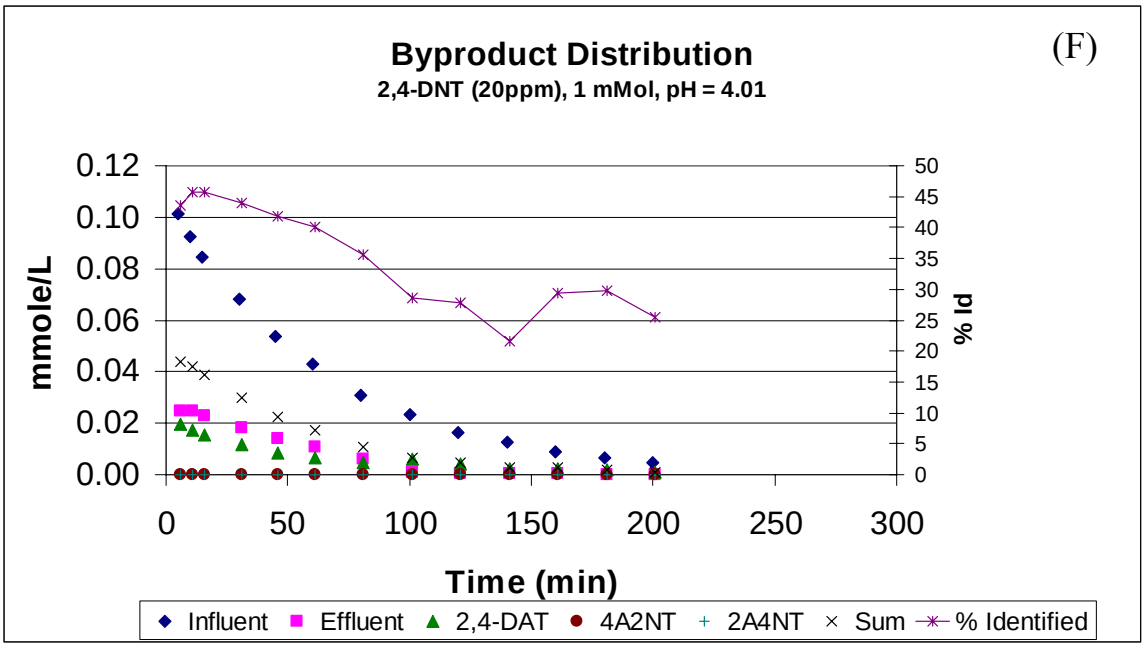


Figure A.5a Exp #5 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.01 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



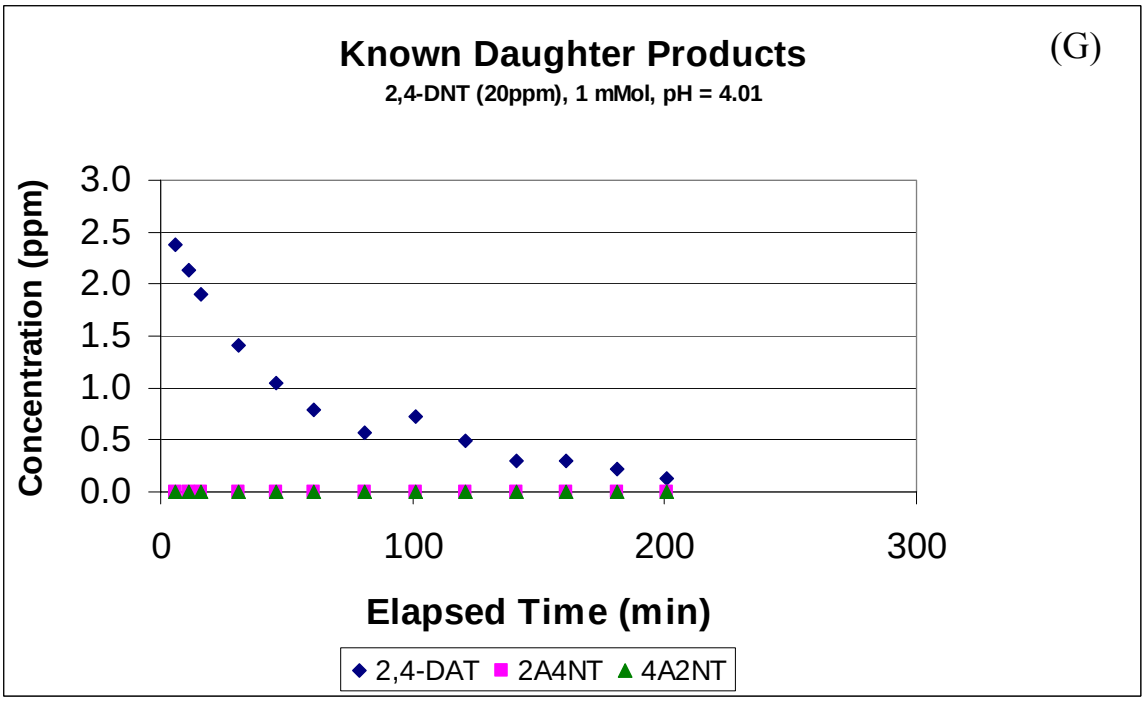


Figure A.5b Exp #5 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.01 (F) Byproduct Distribution (G) Known Daughter Products

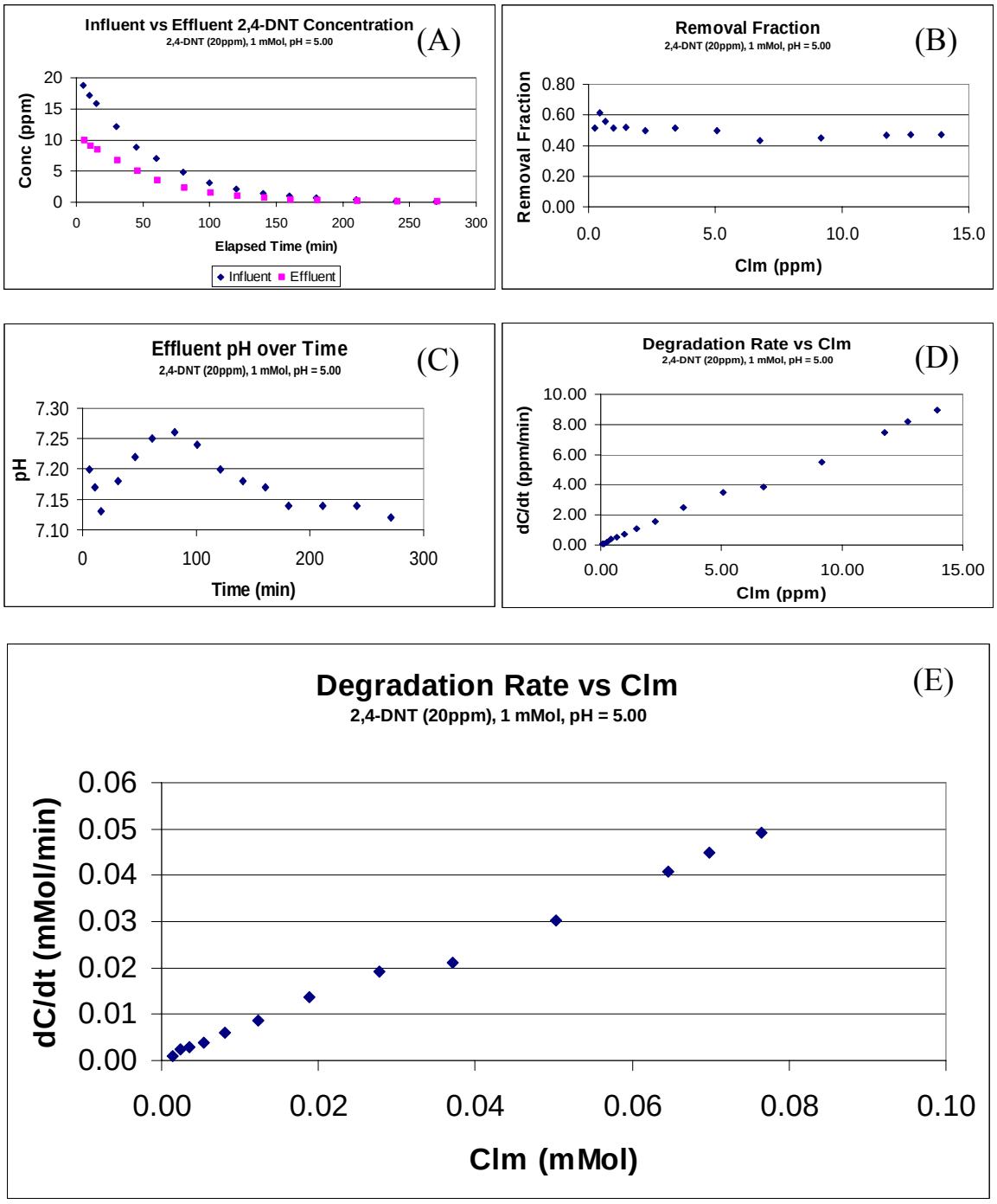
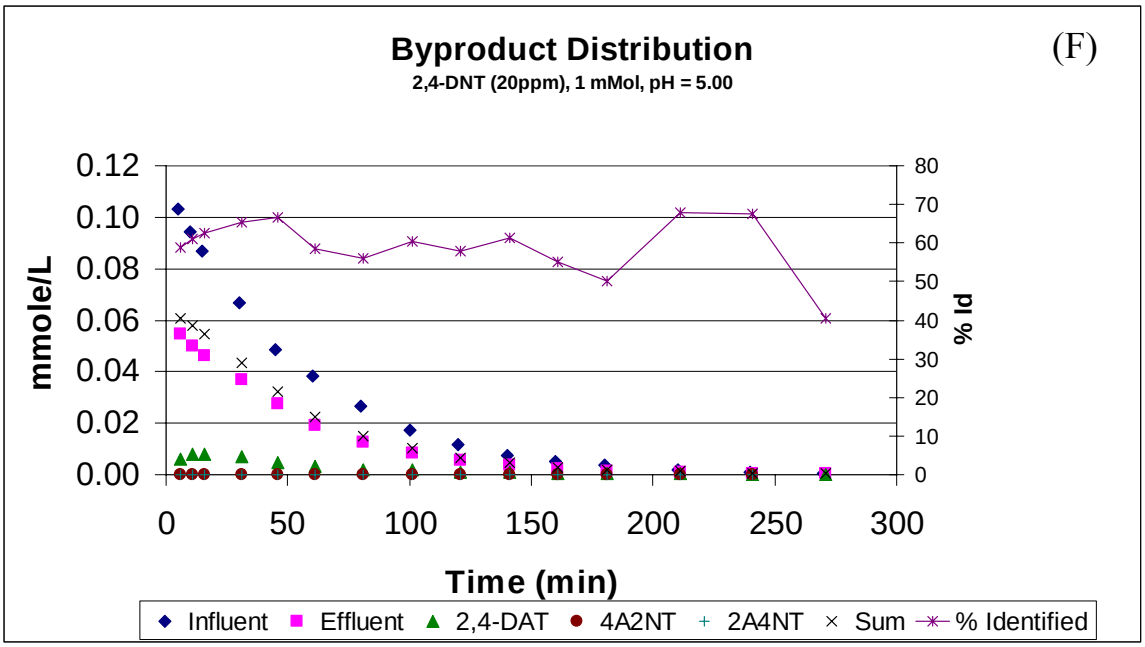


Figure A.6a Exp #6 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 5.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



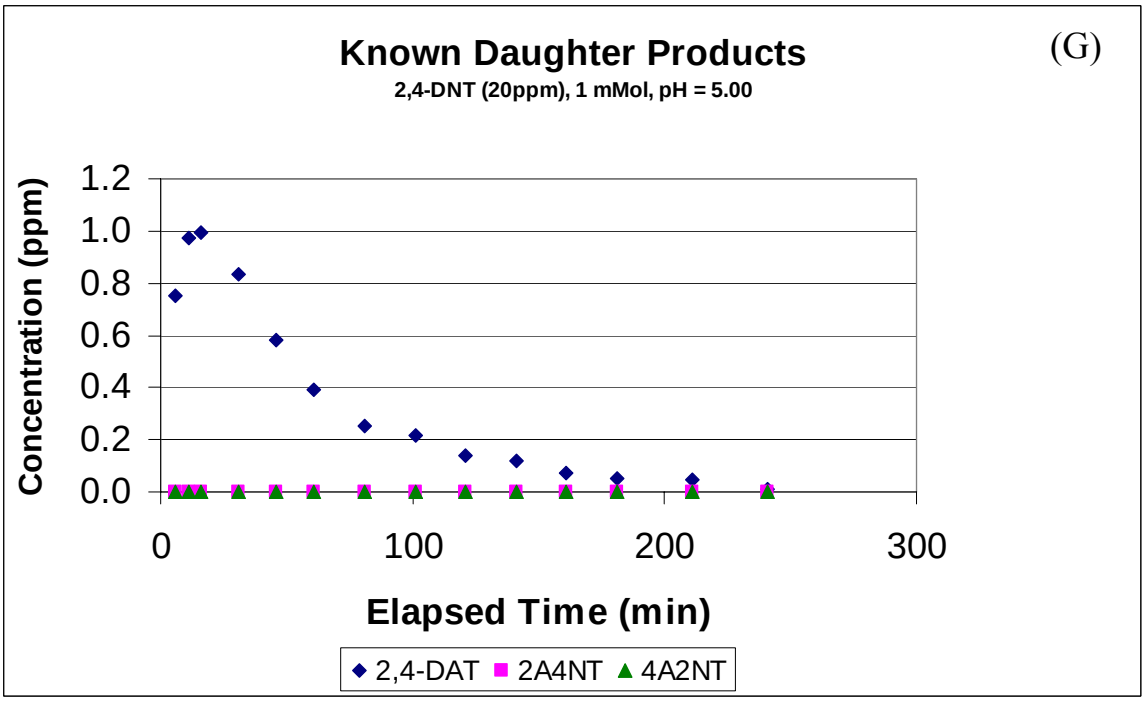


Figure A.6b Exp #6 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 5.00 (F) Byproduct Distribution (G) Known Daughter Products

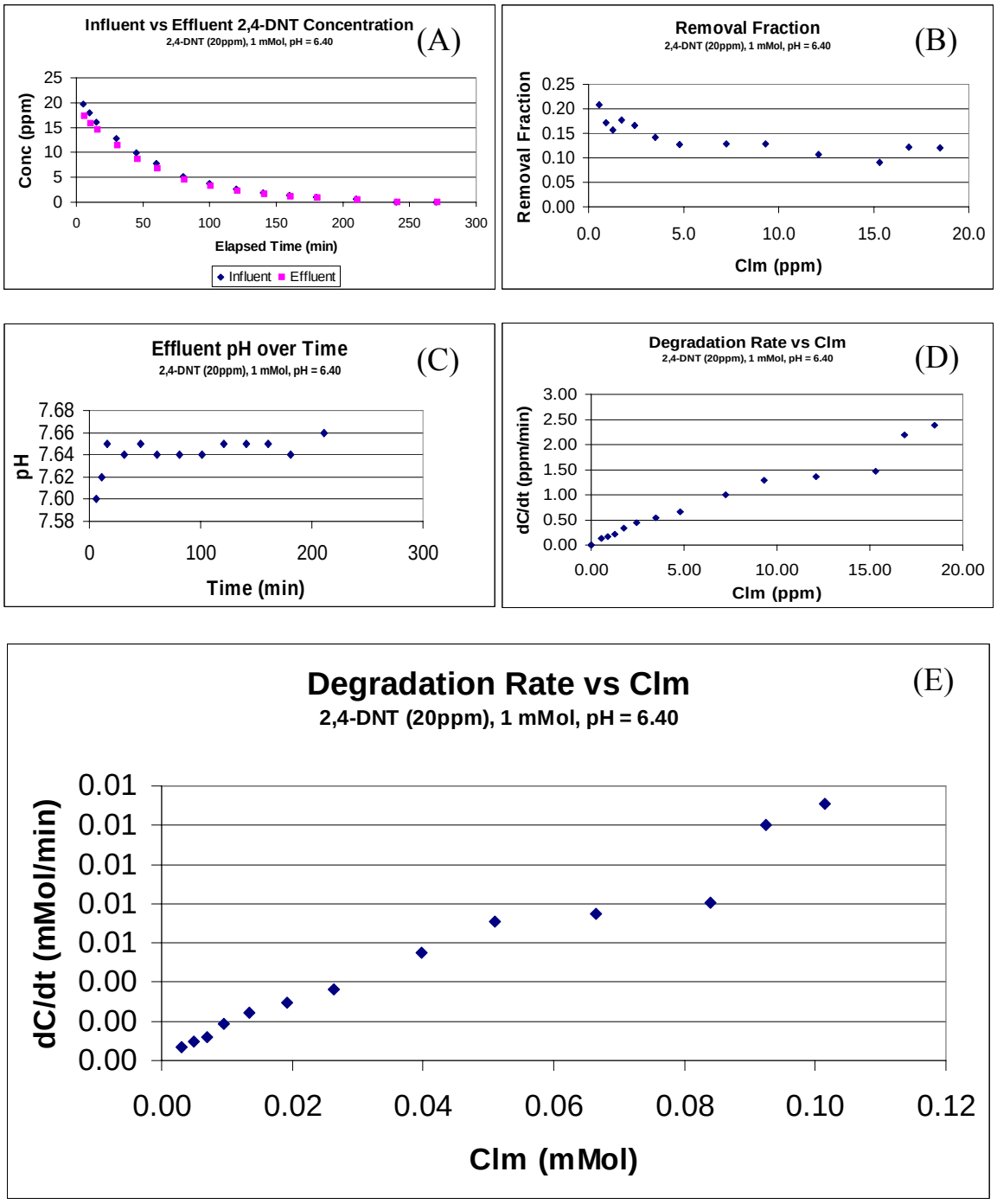
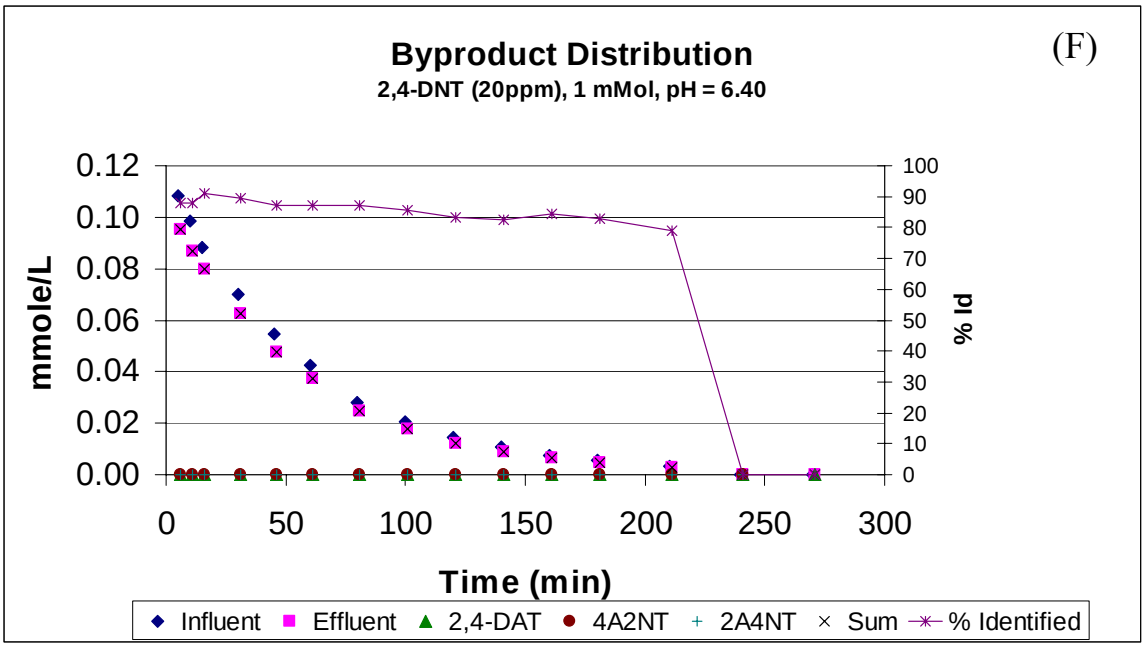


Figure A.7a Exp #7 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 6.40 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



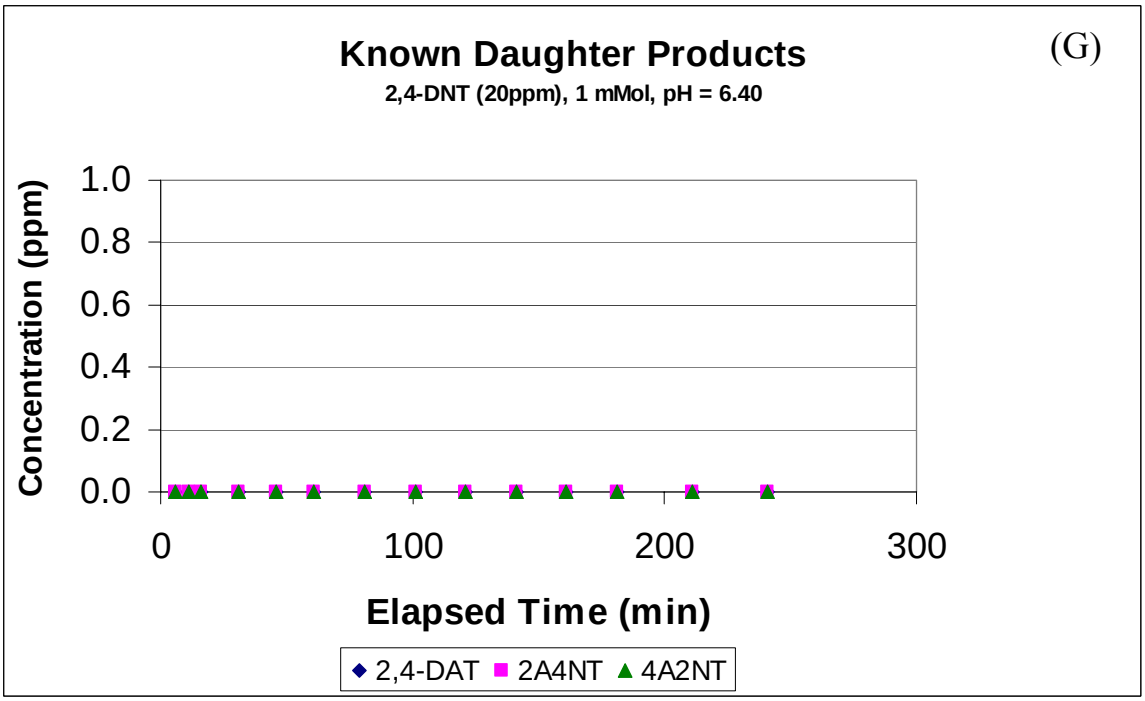


Figure A.7b Exp #7 – 20 ppm 2,4-DNT, 1mMol Formic acid, pH = 6.40 (F) Byproduct Distribution (G) Known Daughter Products

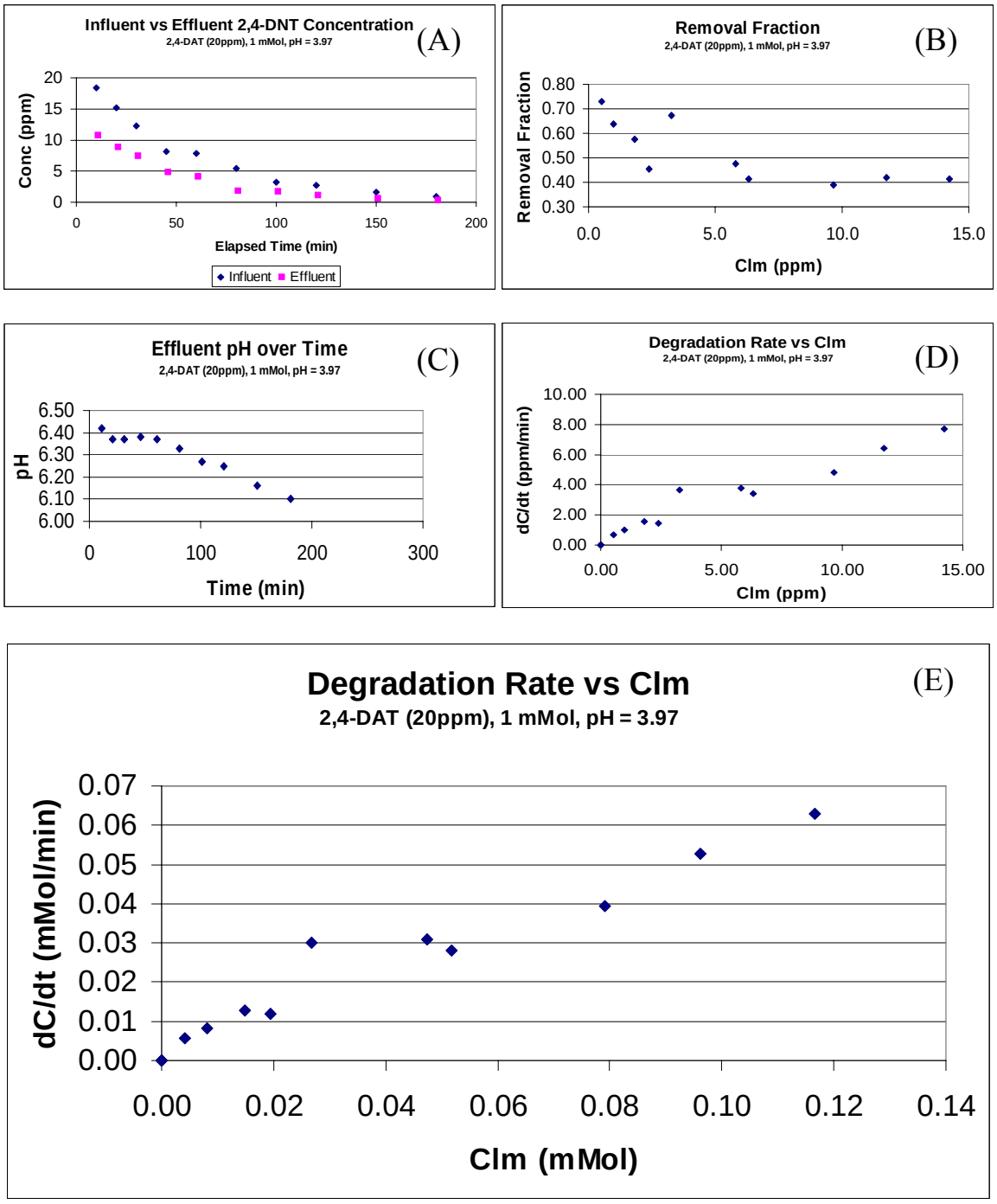


Figure A.8a Exp #8 – 20 ppm 2,4-DAT, 1mMol Formic acid, pH = 3.97 (A) Influent vs. Effluent 2,4-DAT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)

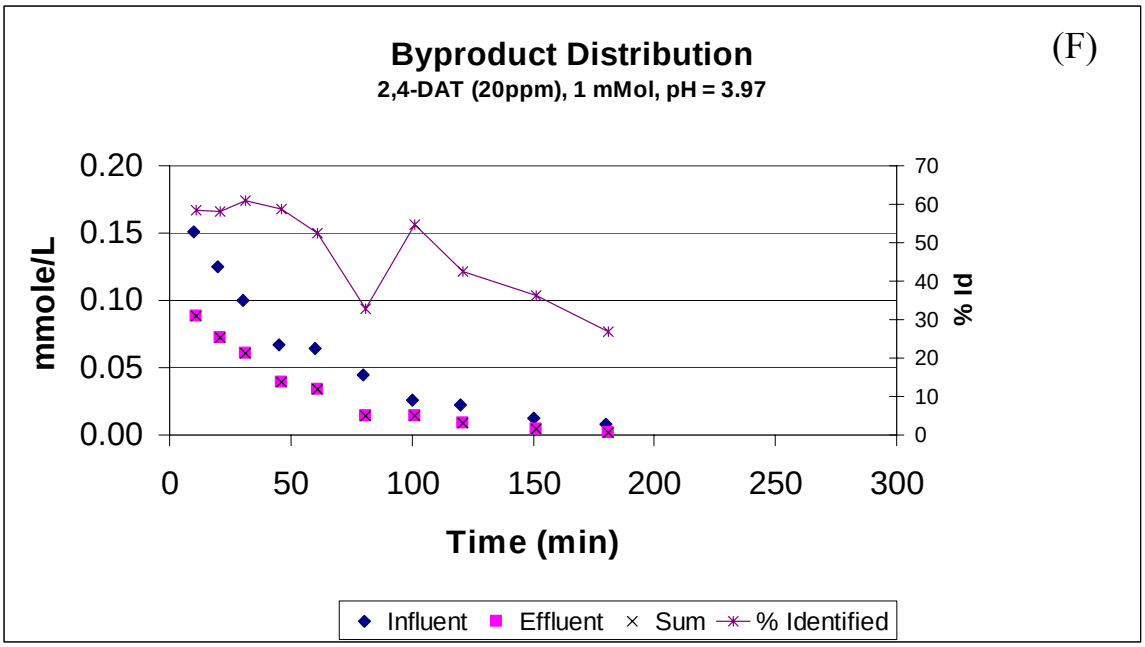


Figure A.8b Exp #8 – 20 ppm 2,4-DAT, 1mMol Formic acid, pH = 6.40 (F) Byproduct Distribution

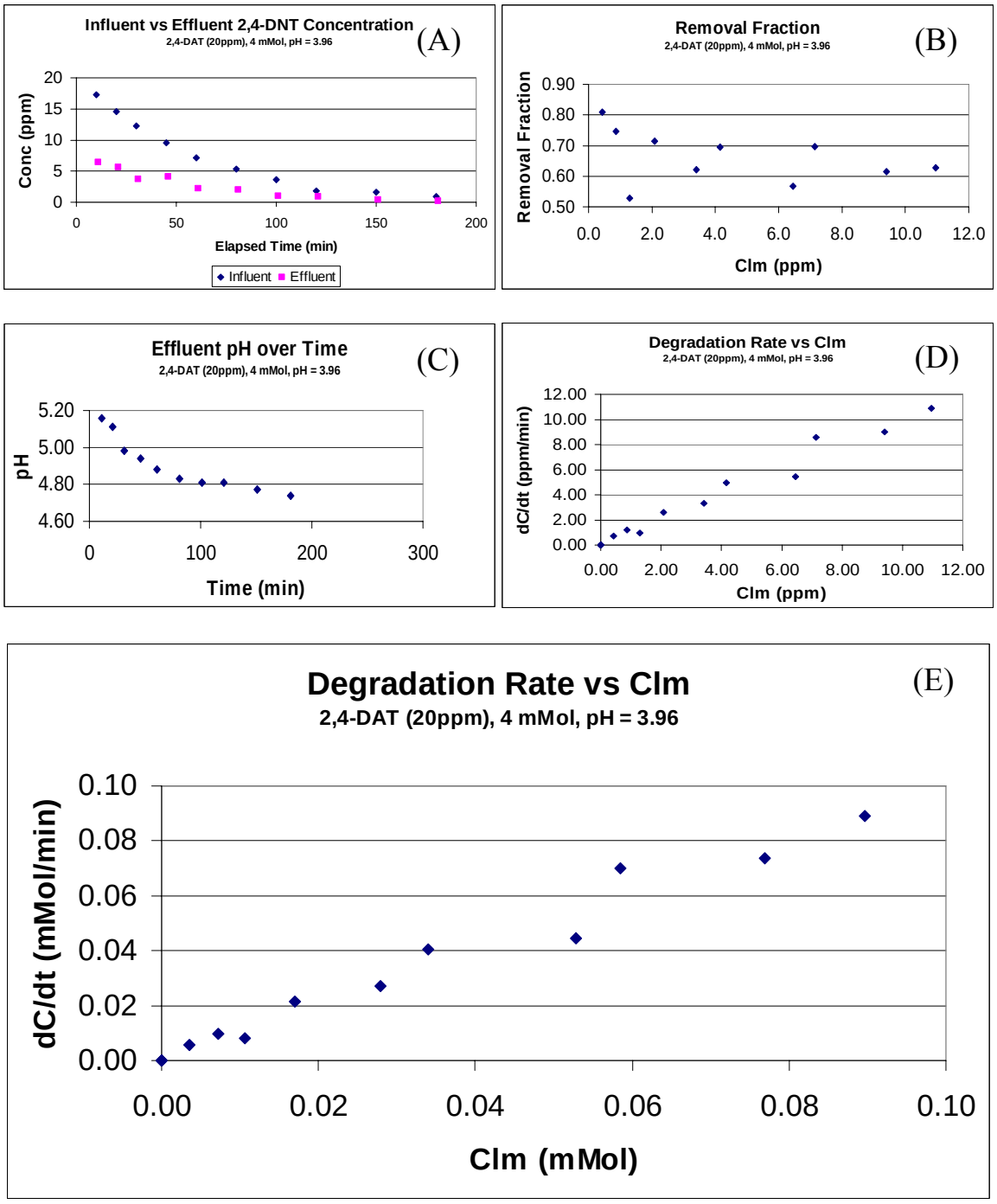
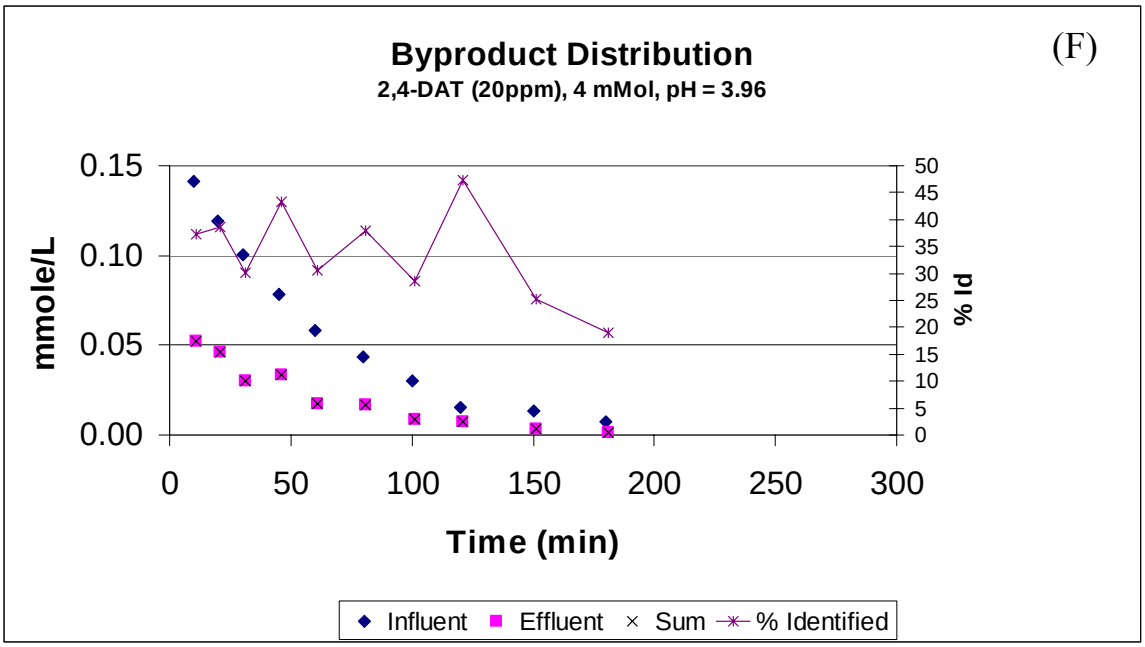


Figure A.9a Exp #9 – 20 ppm 2,4-DAT, 4mMol Formic acid, pH = 3.96 (A) Influent vs. Effluent 2,4-DAT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



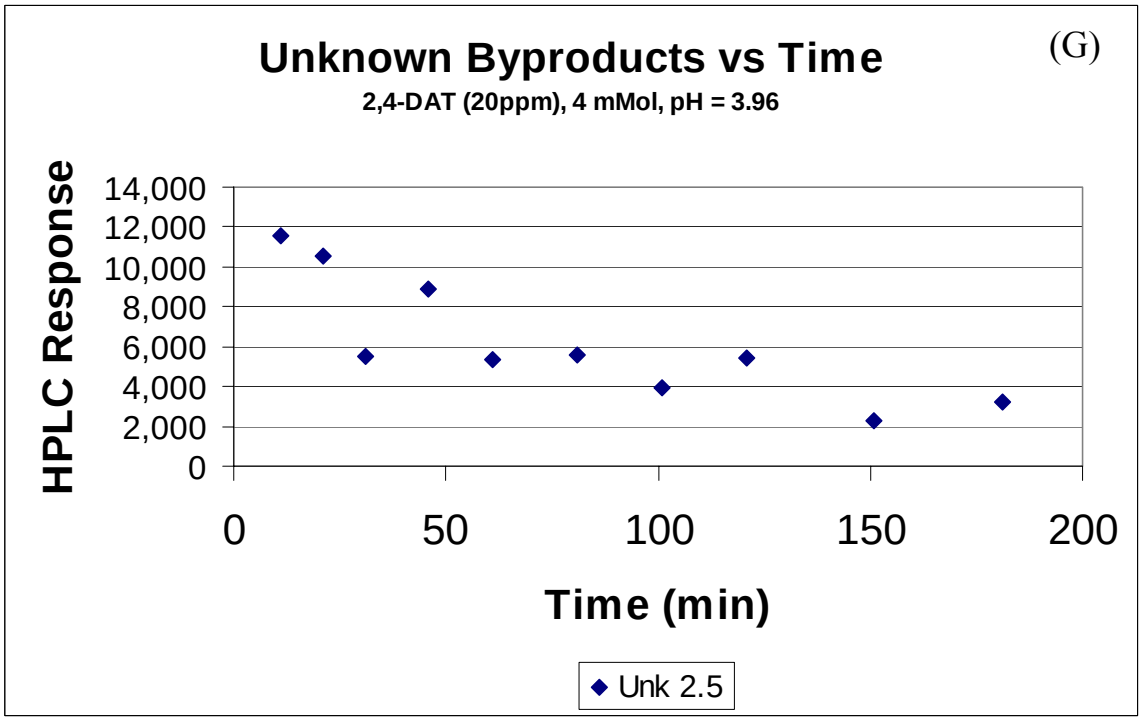


Figure A.9b Exp #9 – 20 ppm 2,4-DAT, 4mMol Formic acid, pH = 3.96 (F) Byproduct Distribution (G) Unknown Byproduct Response

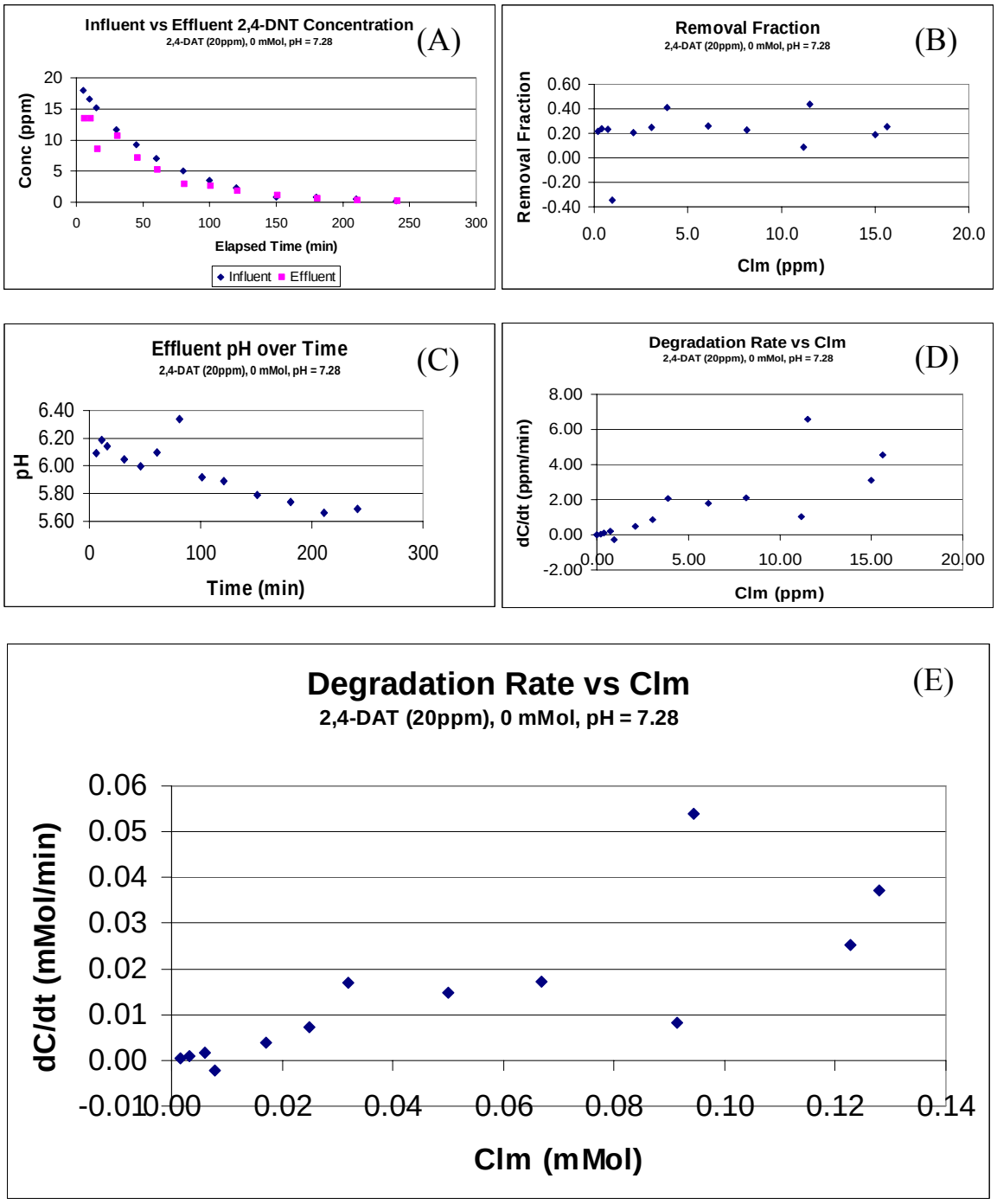


Figure A.10a Exp #10 – 20 ppm 2,4-DAT, 0mMol Formic acid, pH = 7.28 (A) Influent vs. Effluent 2,4-DAT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)

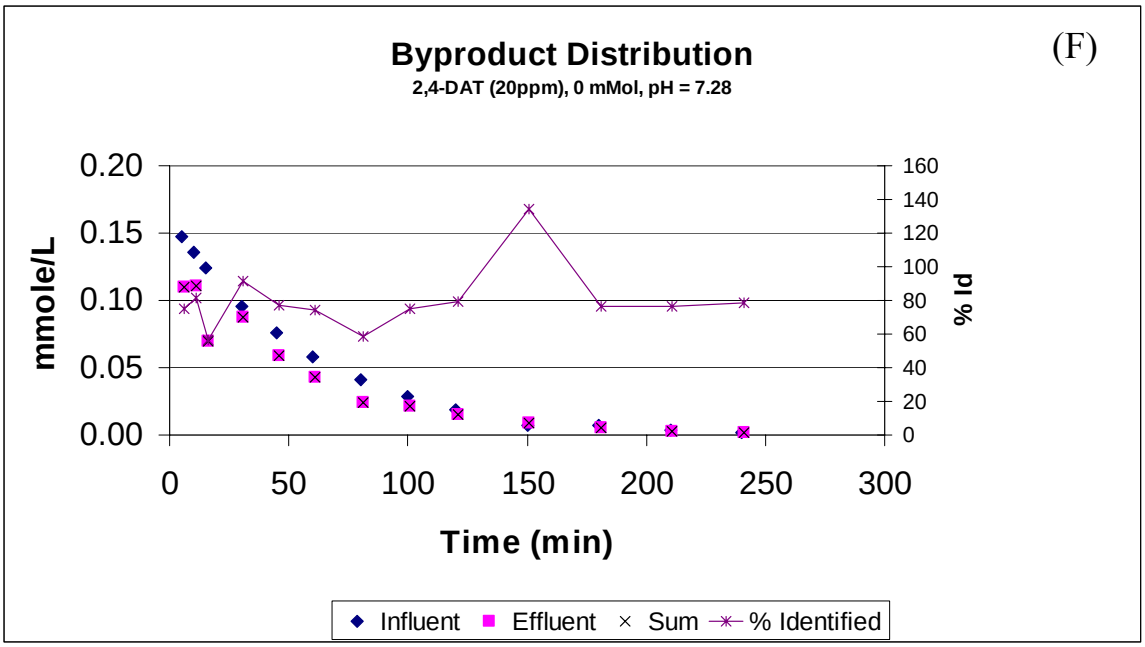


Figure A.10b Exp #10 – 20 ppm 2,4-DAT, 1mMol Formic acid, pH = 7.28 (F) Byproduct Distribution

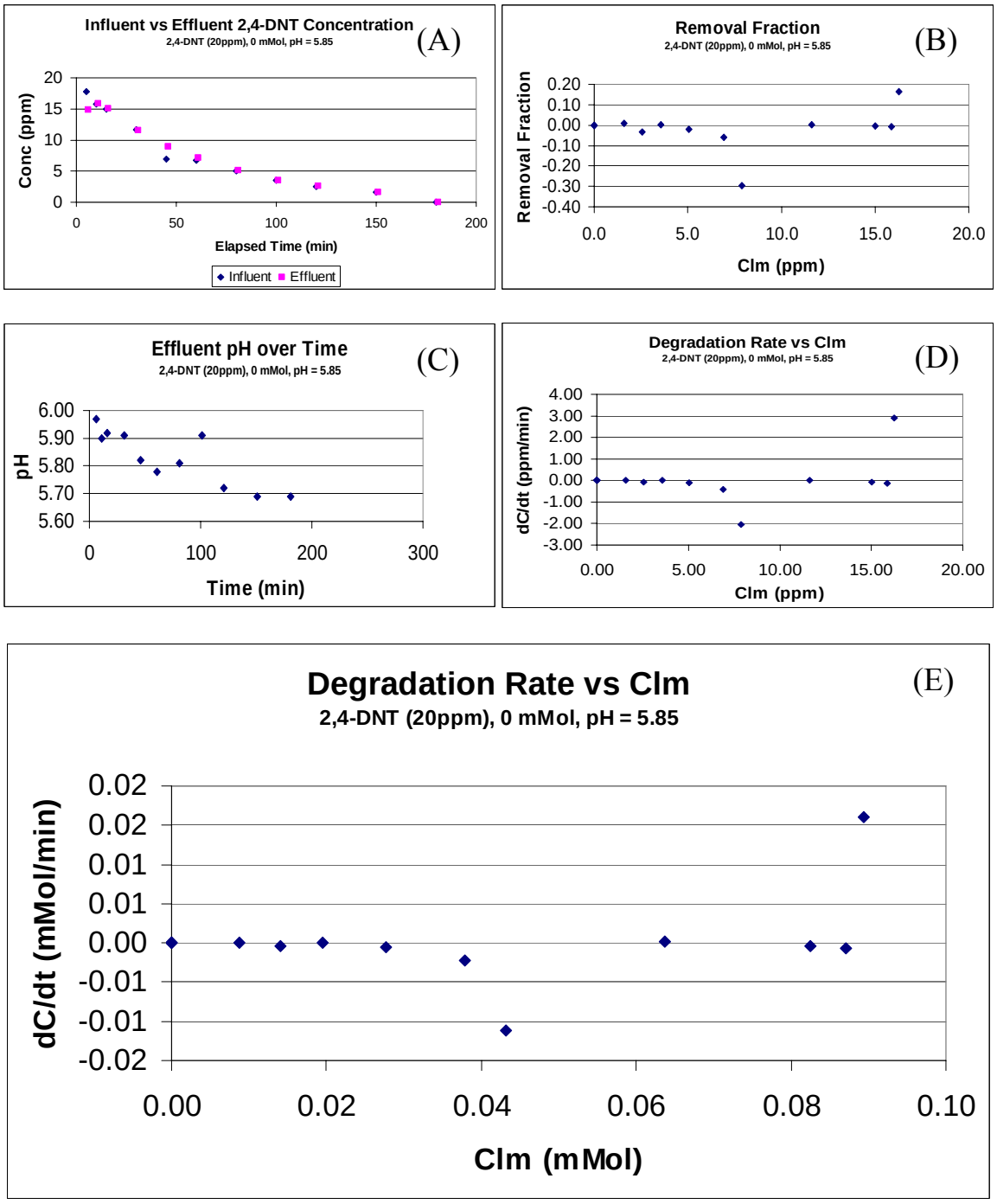
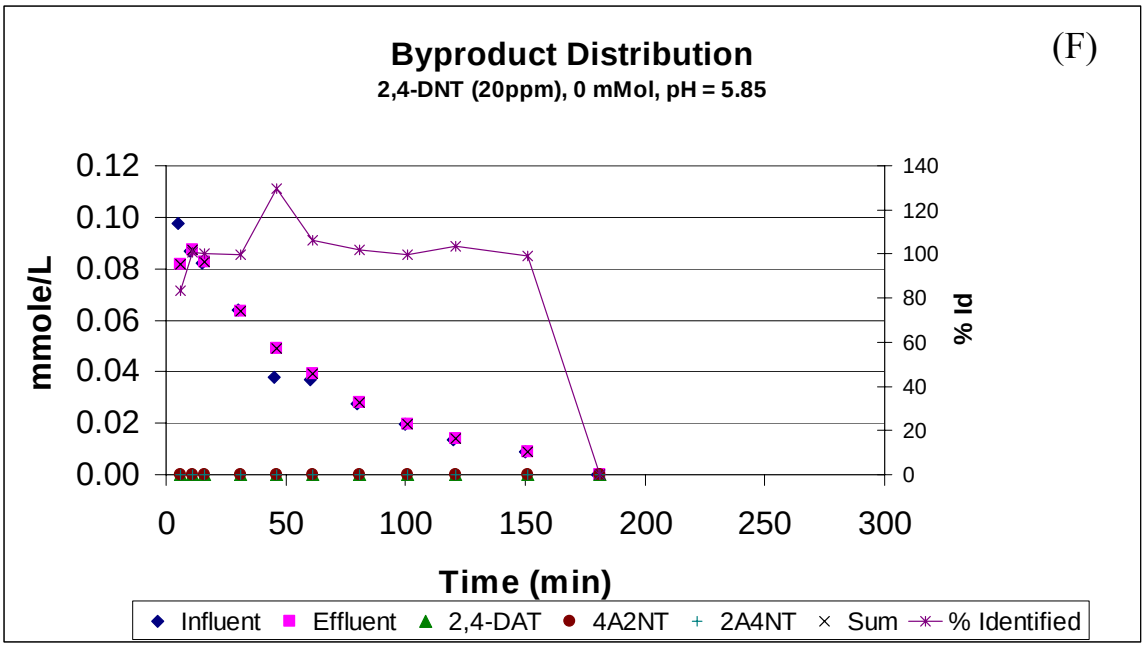


Figure A.11a Exp #11 – 20 ppm 2,4-DNT, 0mMol Formic acid, pH = 5.85 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



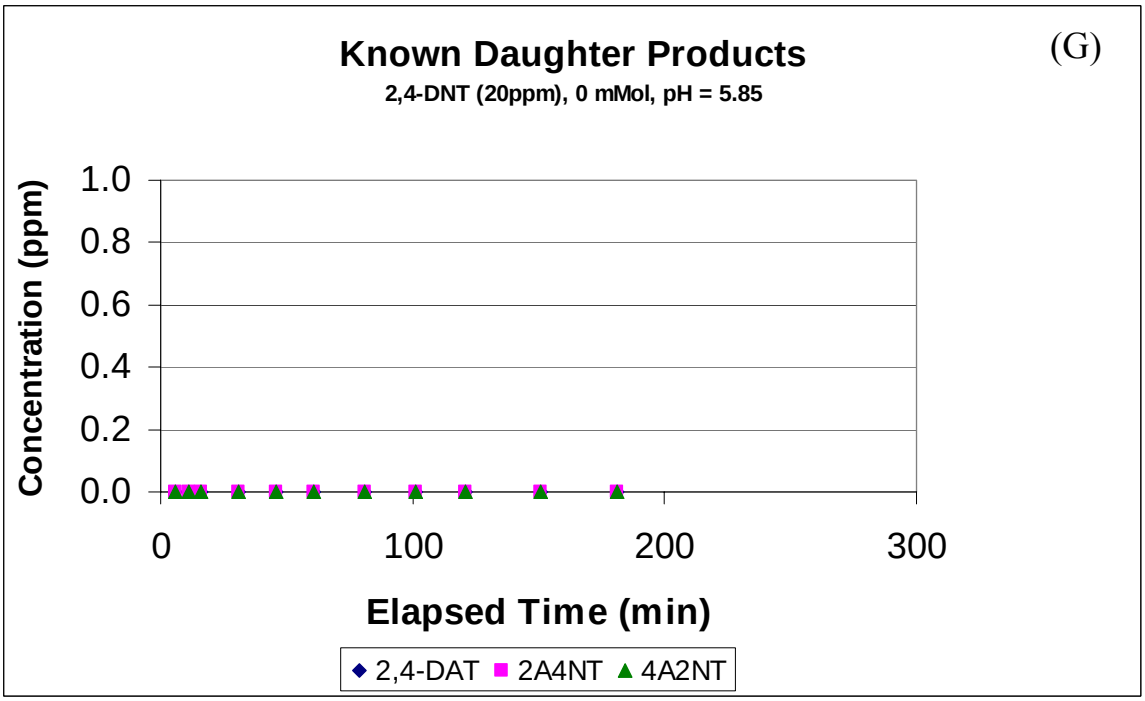


Figure A.11b Exp #11 – 20 ppm 2,4-DNT, 0mMol Formic acid, pH = 5.85 (F) Byproduct Distribution (G) Known Daughter Products

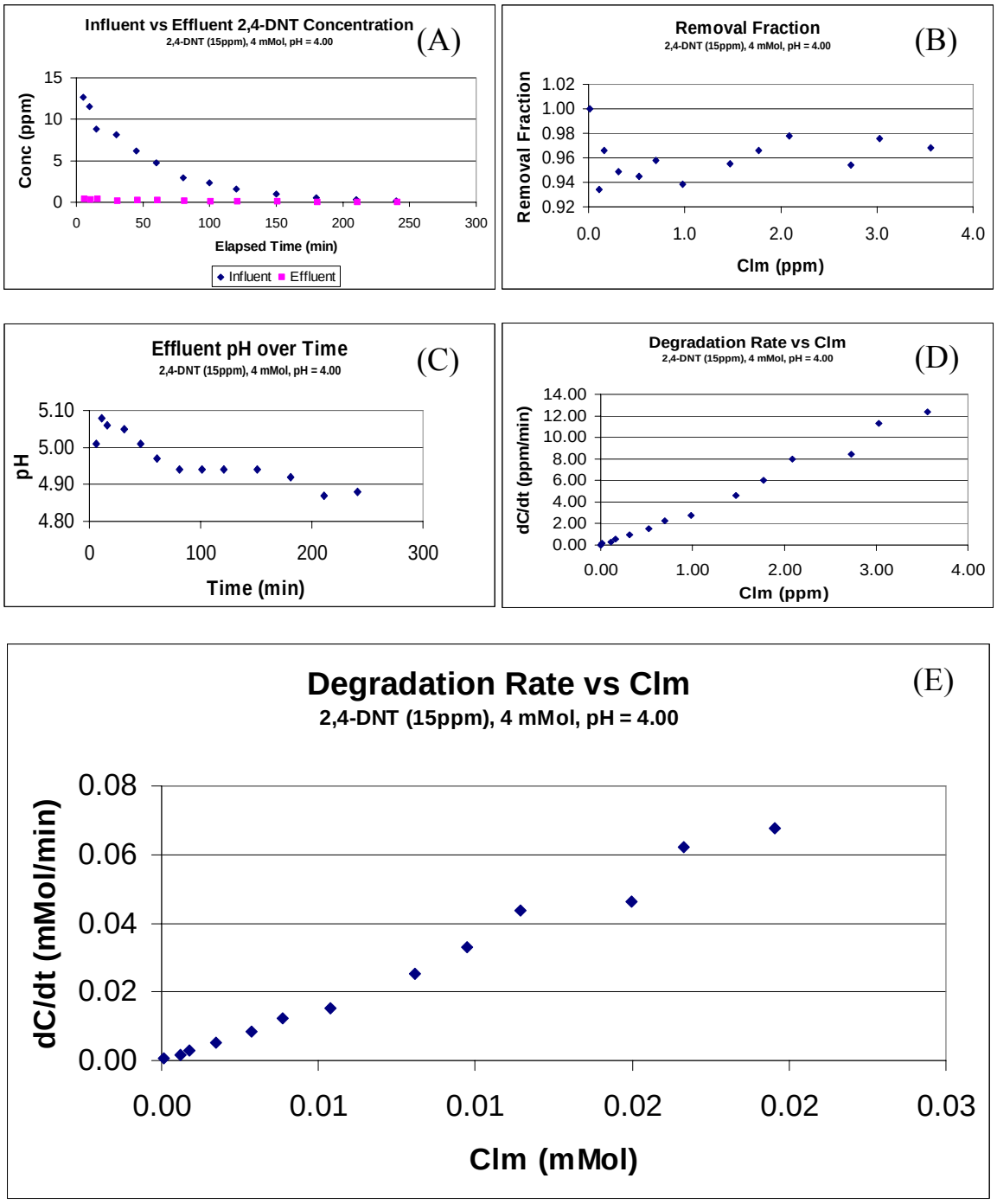
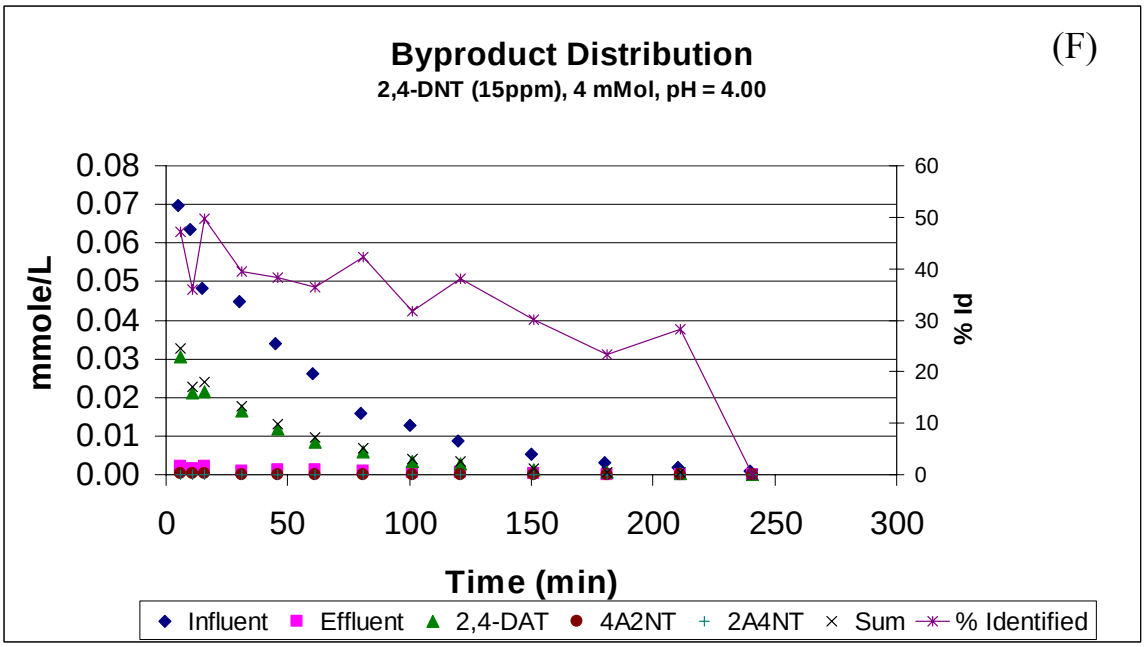


Figure A.12a Exp #12 – 15 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



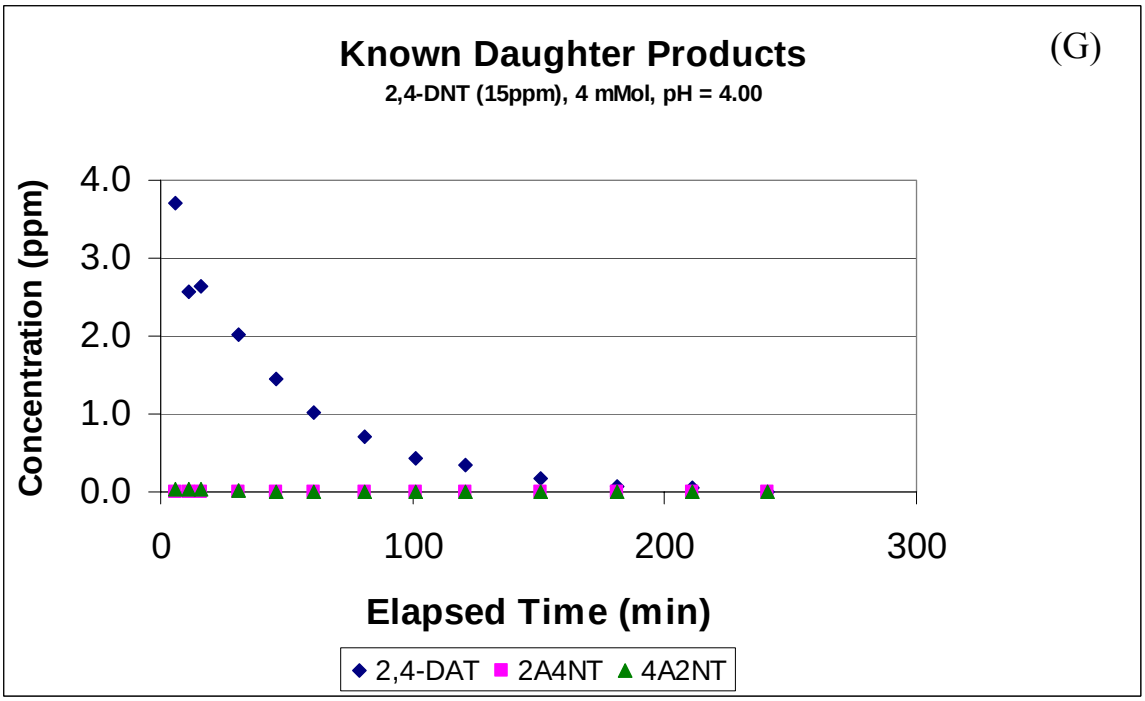


Figure A.12b Exp #12 – 15 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

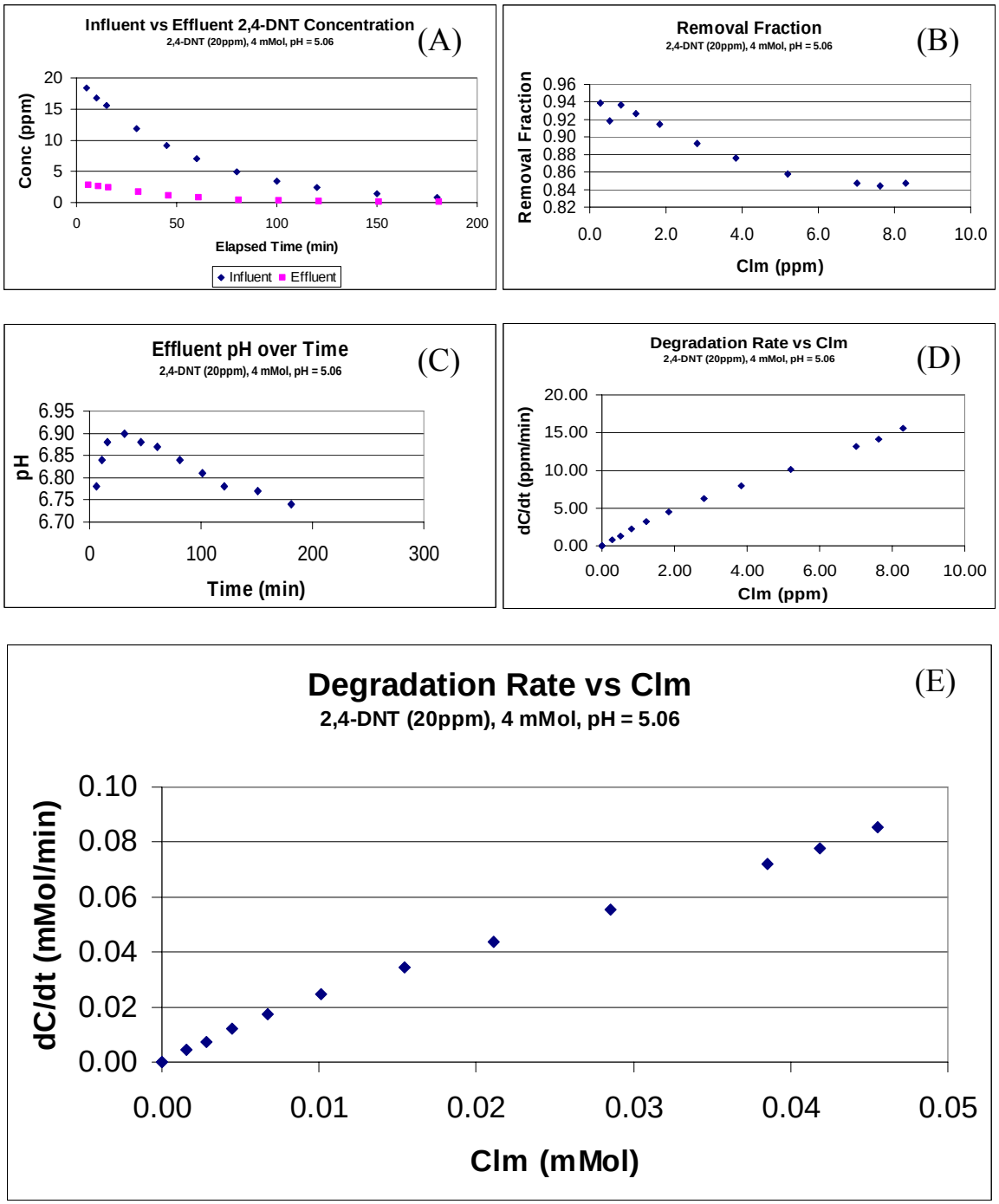
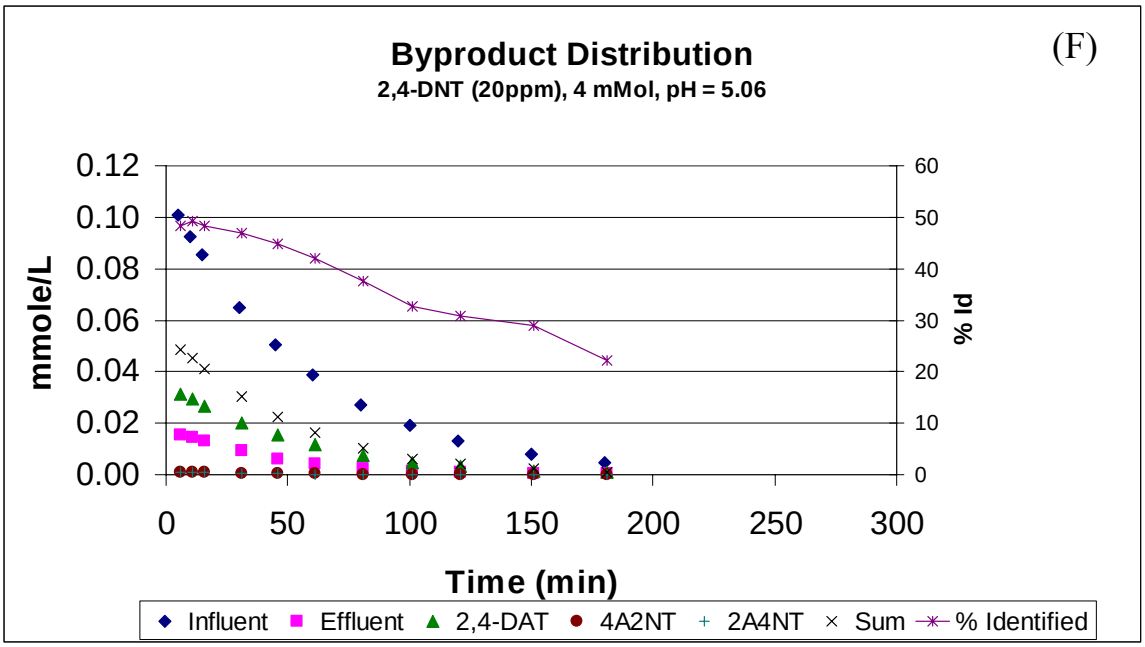


Figure A.13a Exp #13 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 5.06 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



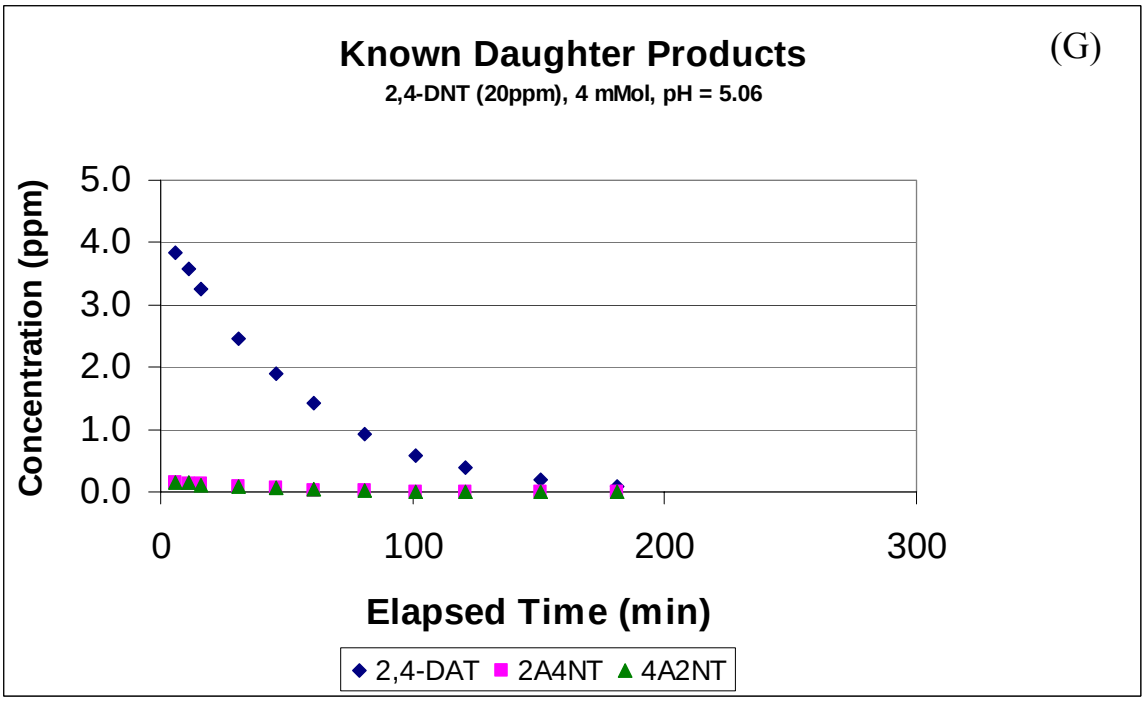


Figure A.13b Exp #13 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 5.06 (F) Byproduct Distribution (G) Known Daughter Products

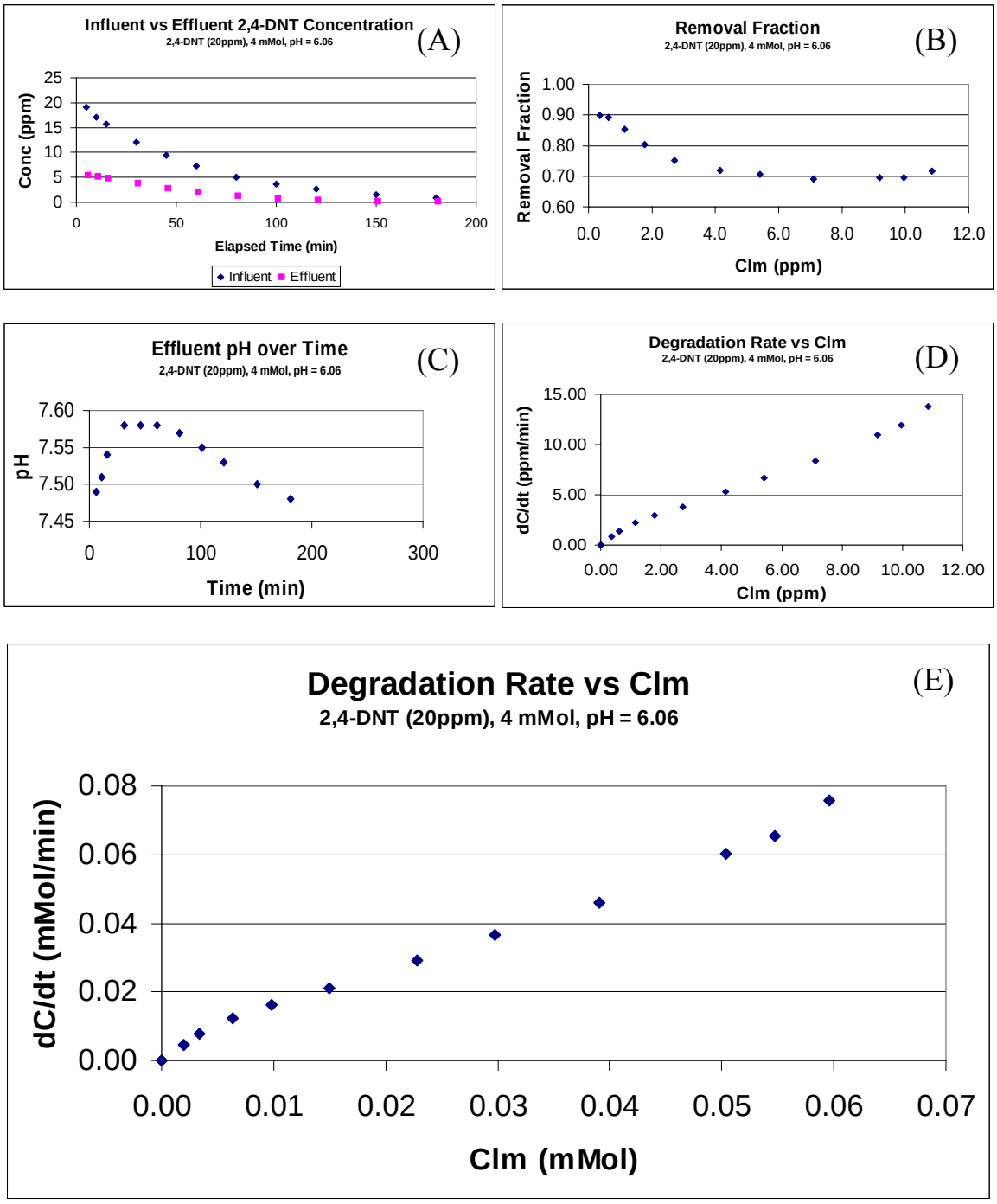
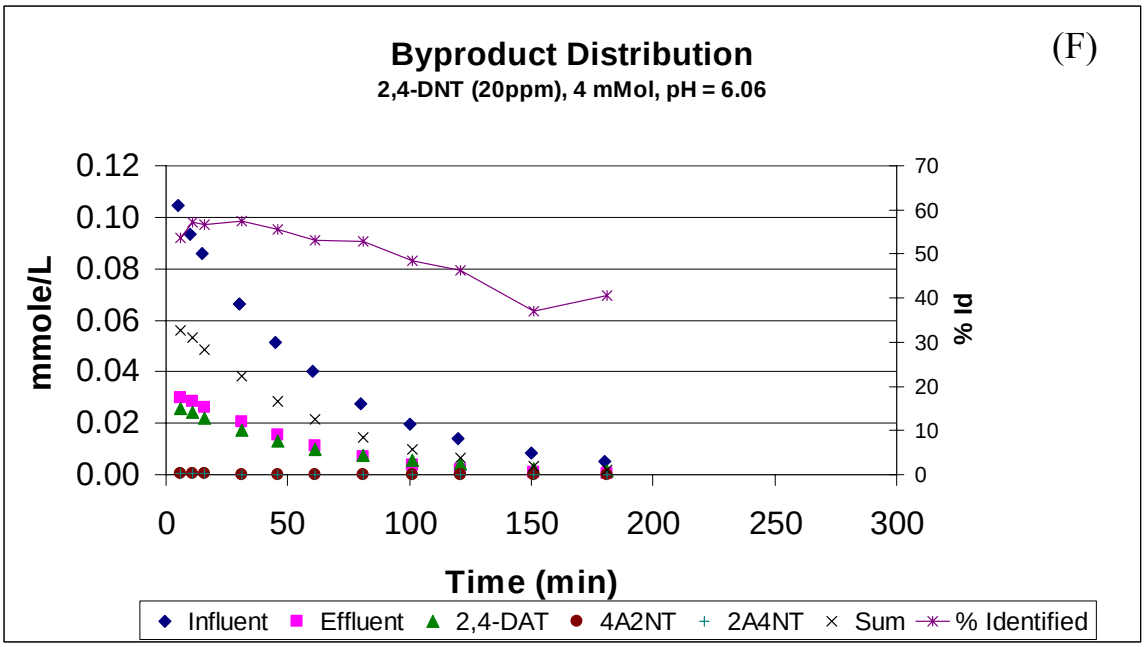


Figure A.14a Exp #14 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 6.06 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



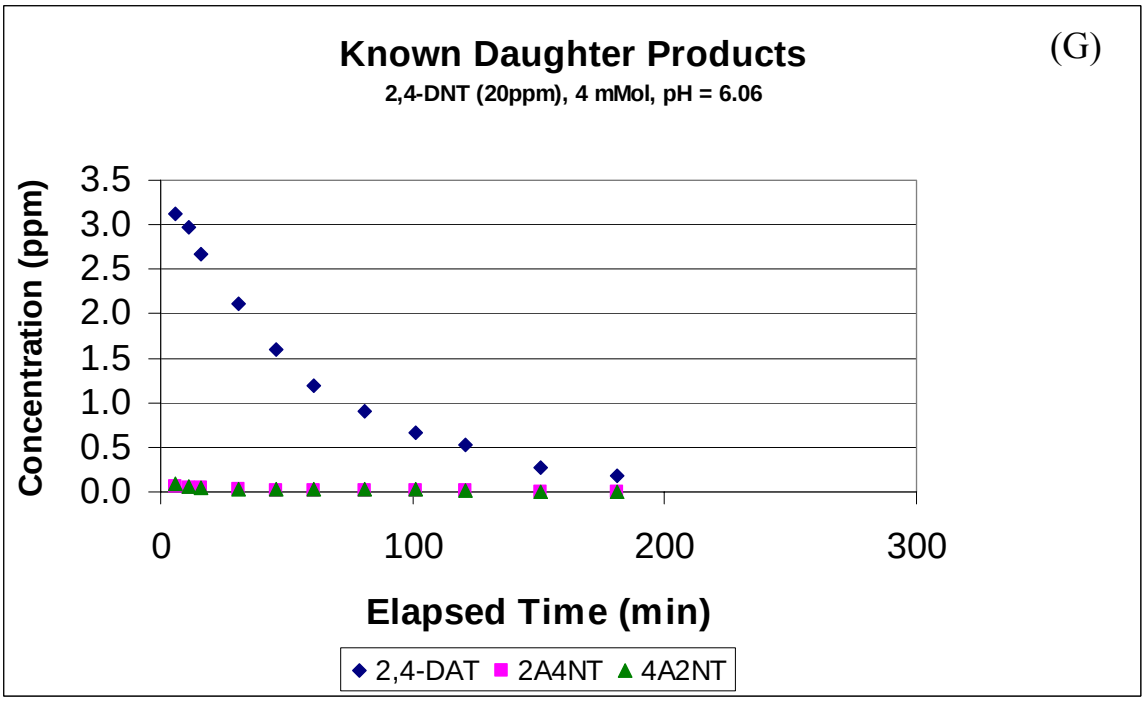


Figure A.14b Exp #14 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 6.06 (F) Byproduct Distribution (G) Known Daughter Products

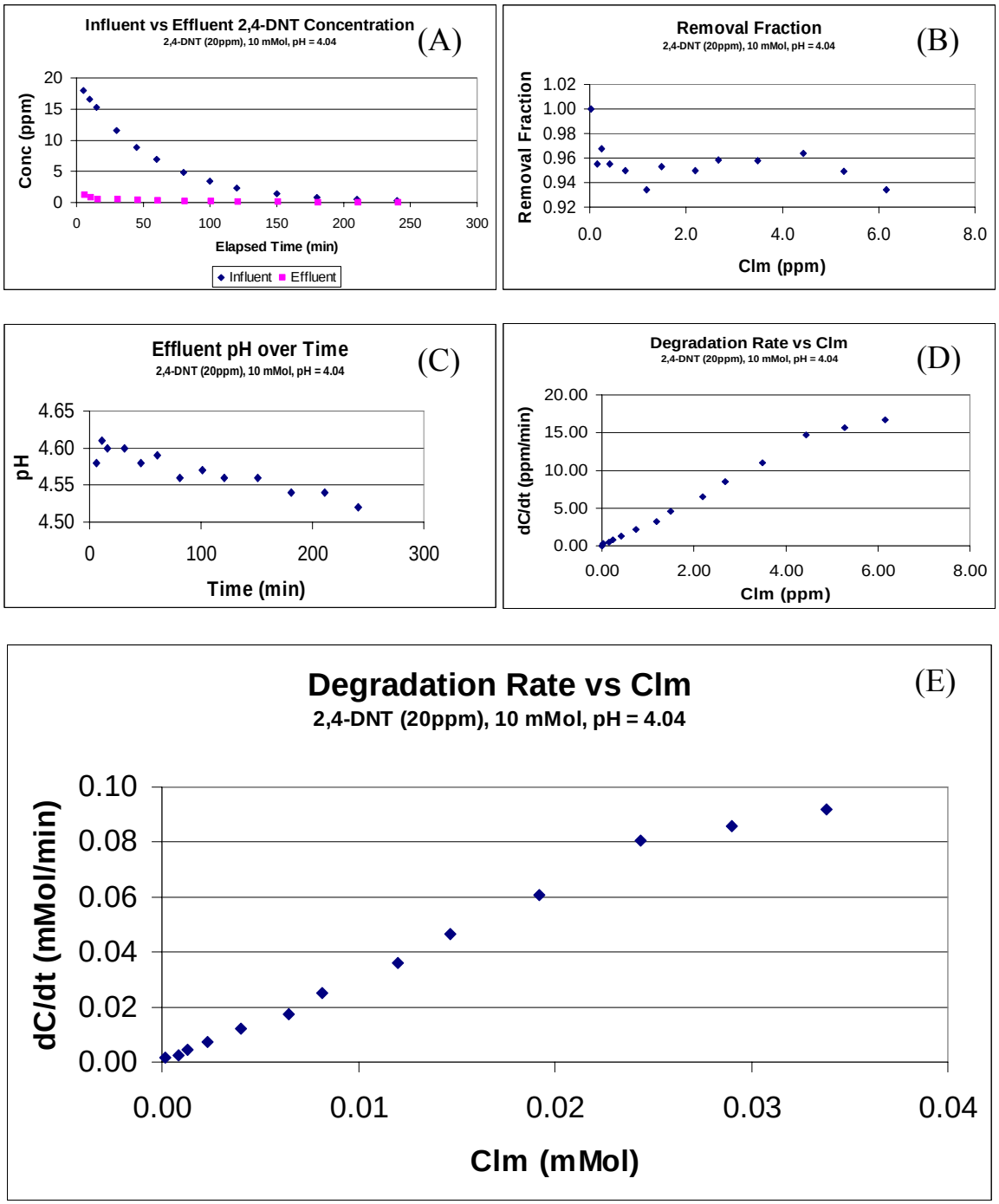
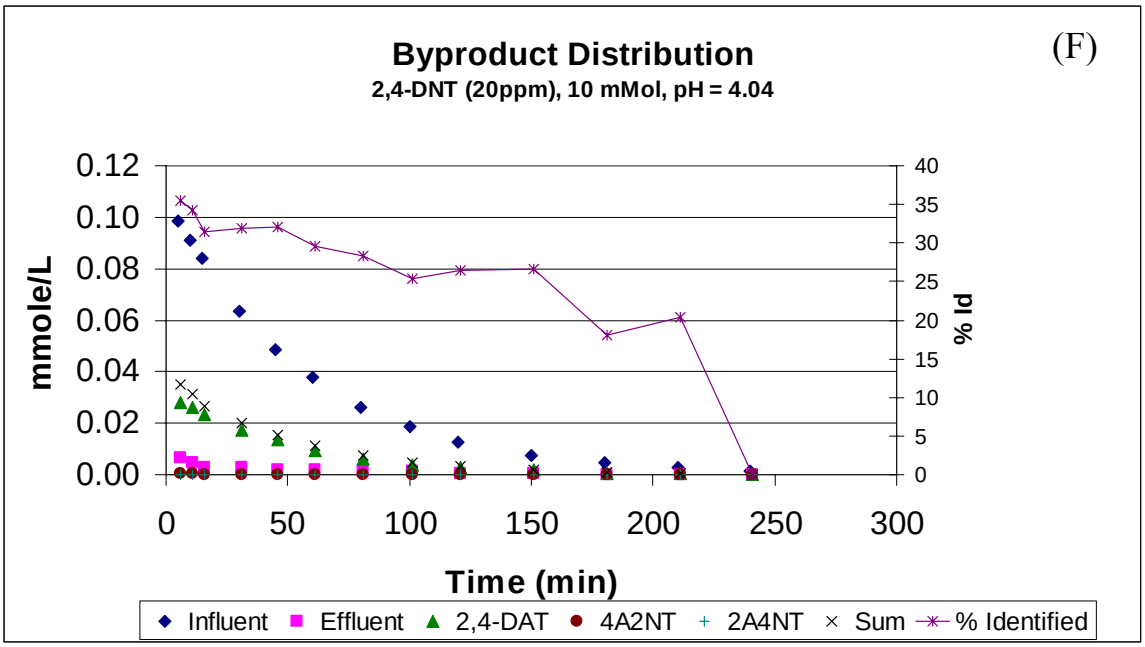


Figure A.15a Exp #15 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.04 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



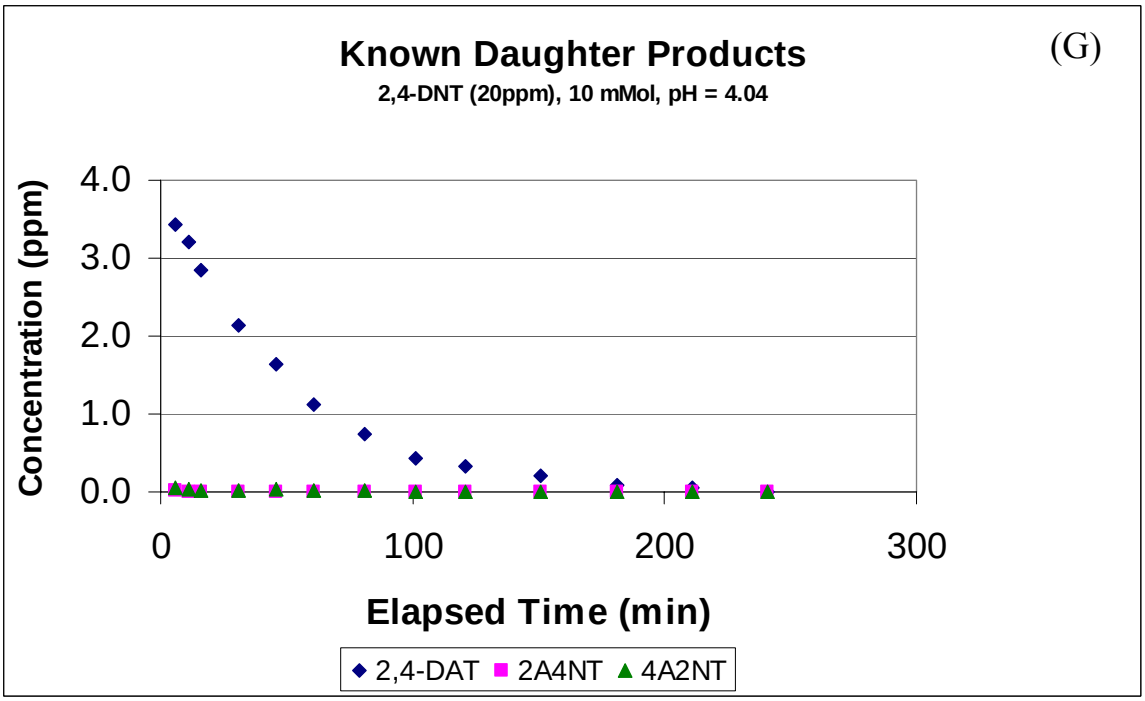


Figure A.15b Exp #15 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.04 (F) Byproduct Distribution (G) Known Daughter Products

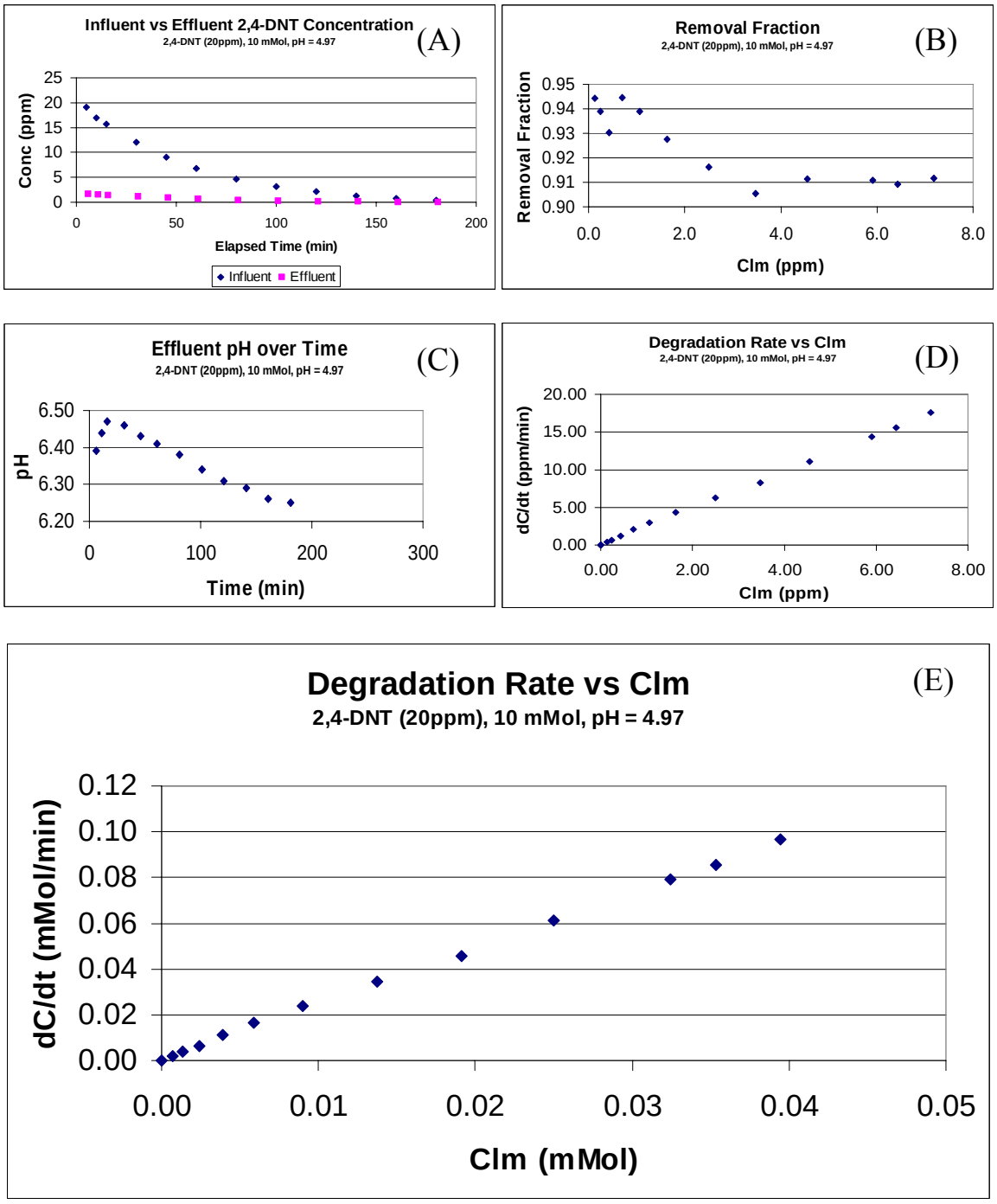
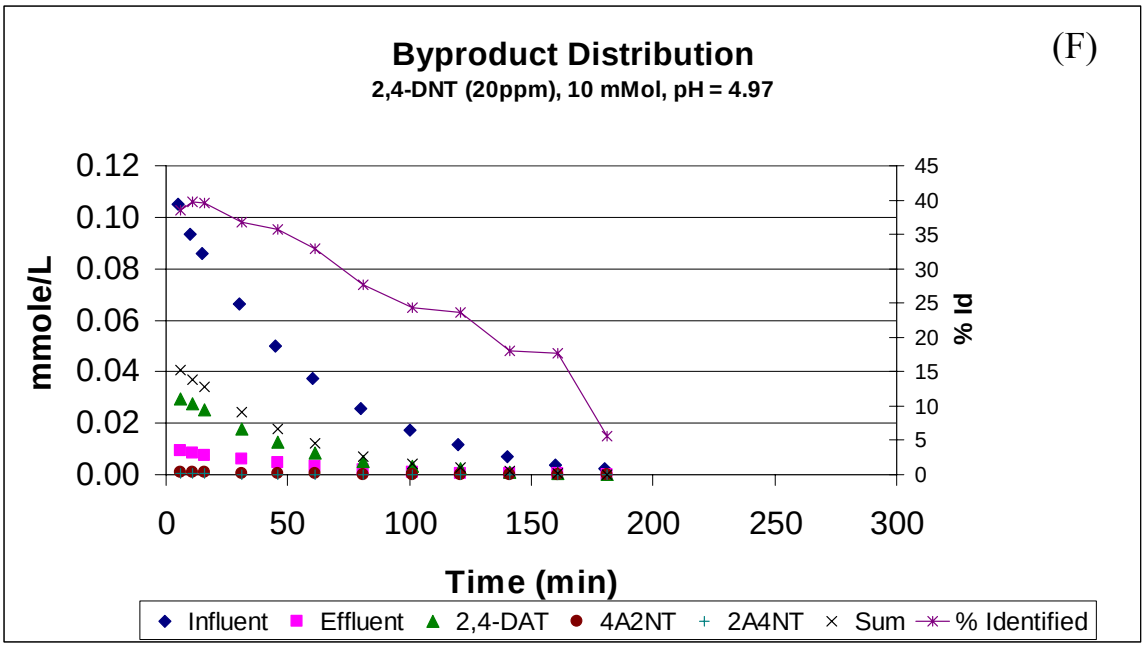


Figure A.16a Exp #16 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.97 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



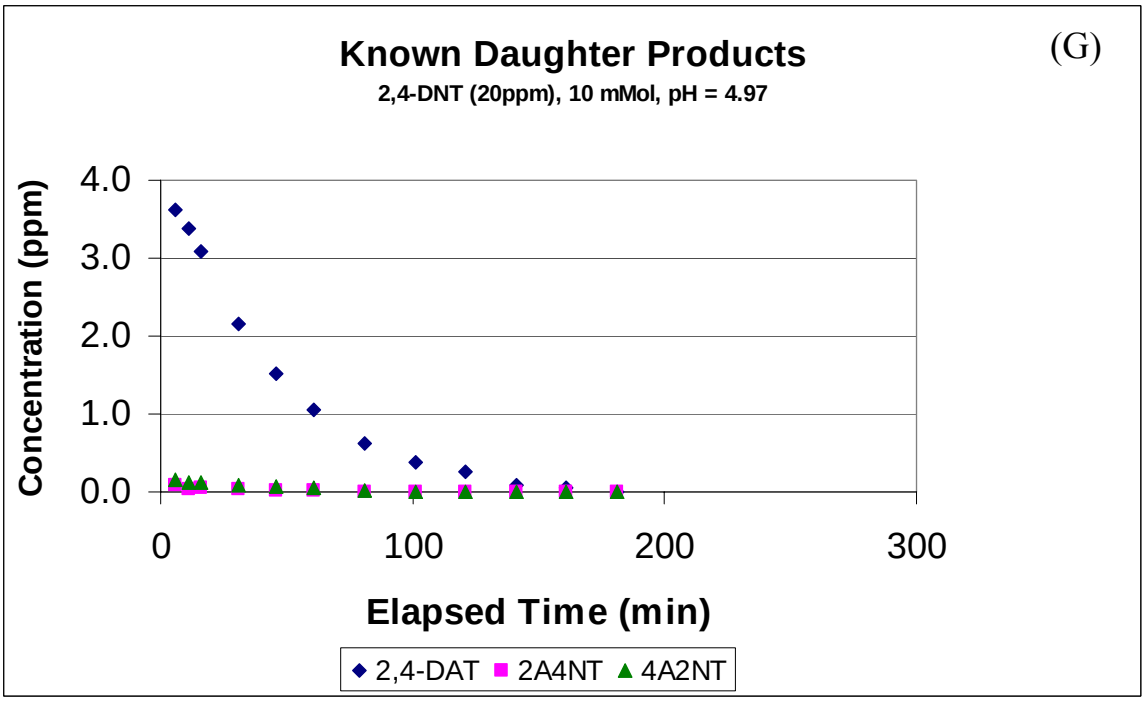


Figure A.16b Exp #16 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.97 (F) Byproduct Distribution (G) Known Daughter Products

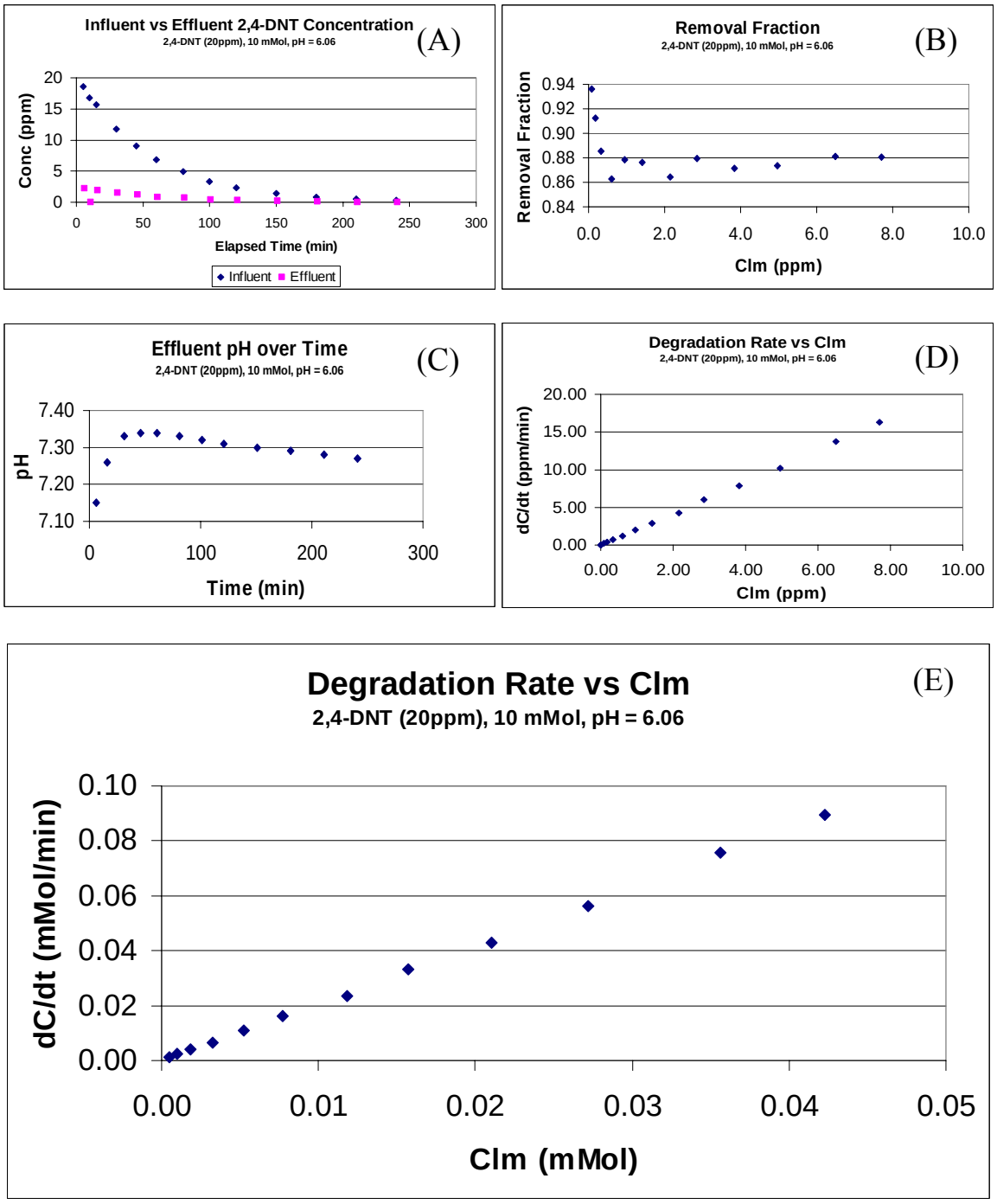
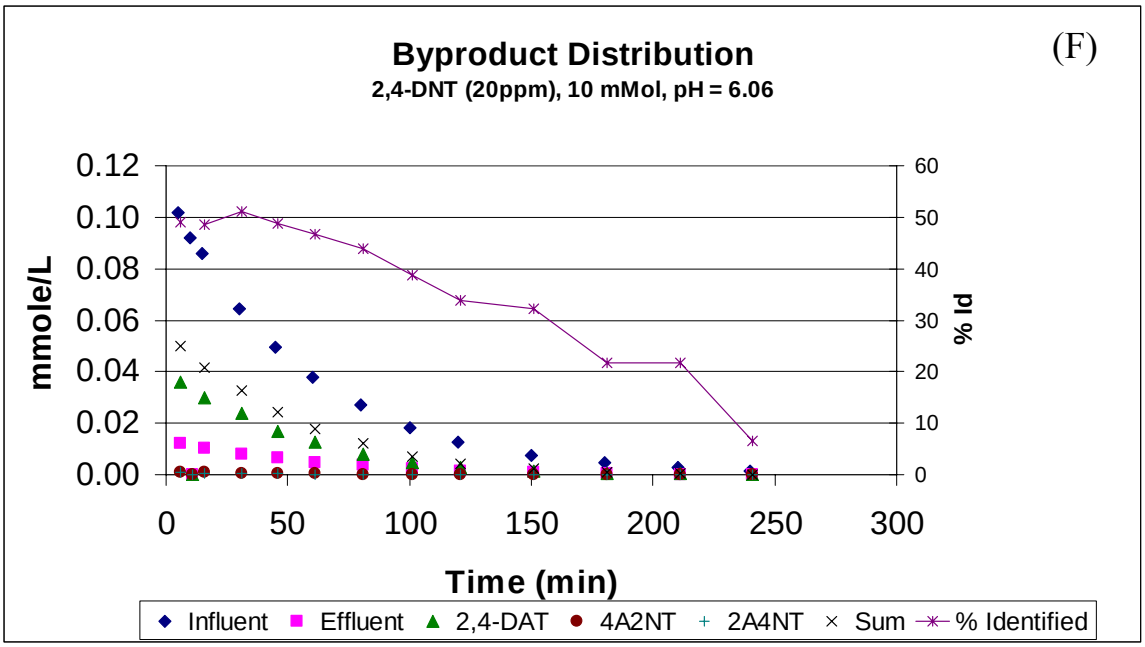


Figure A.17a Exp #17 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 6.06 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



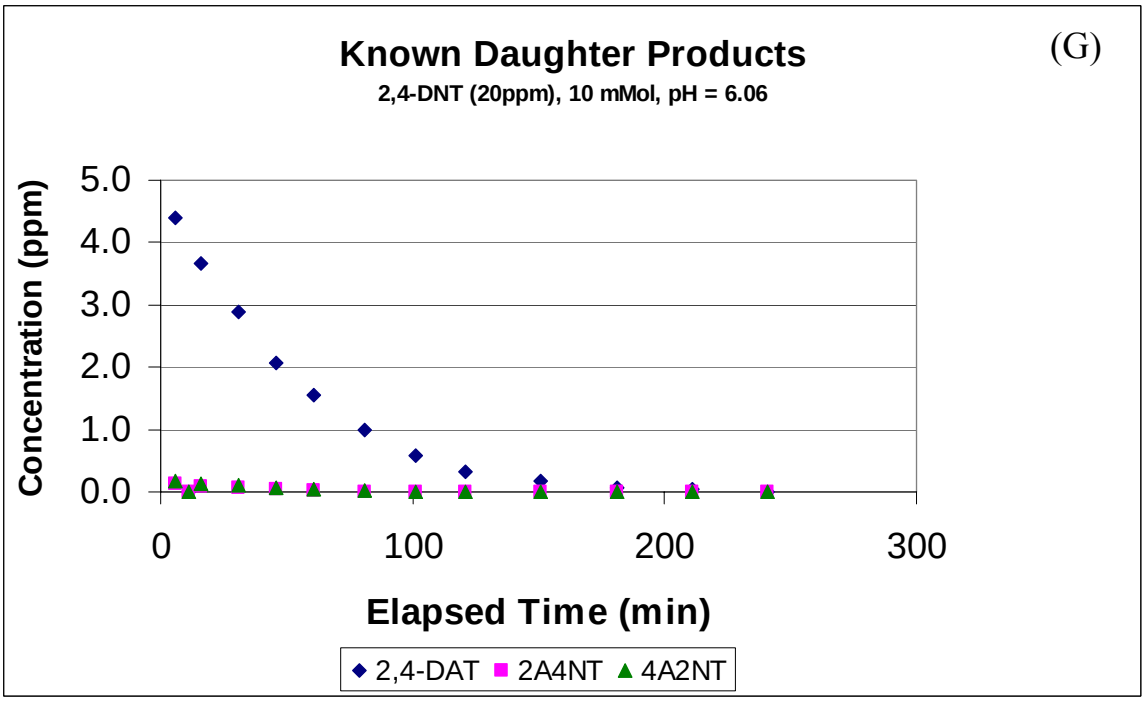


Figure A.17b Exp #17 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 6.06 (F) Byproduct Distribution (G) Known Daughter Products

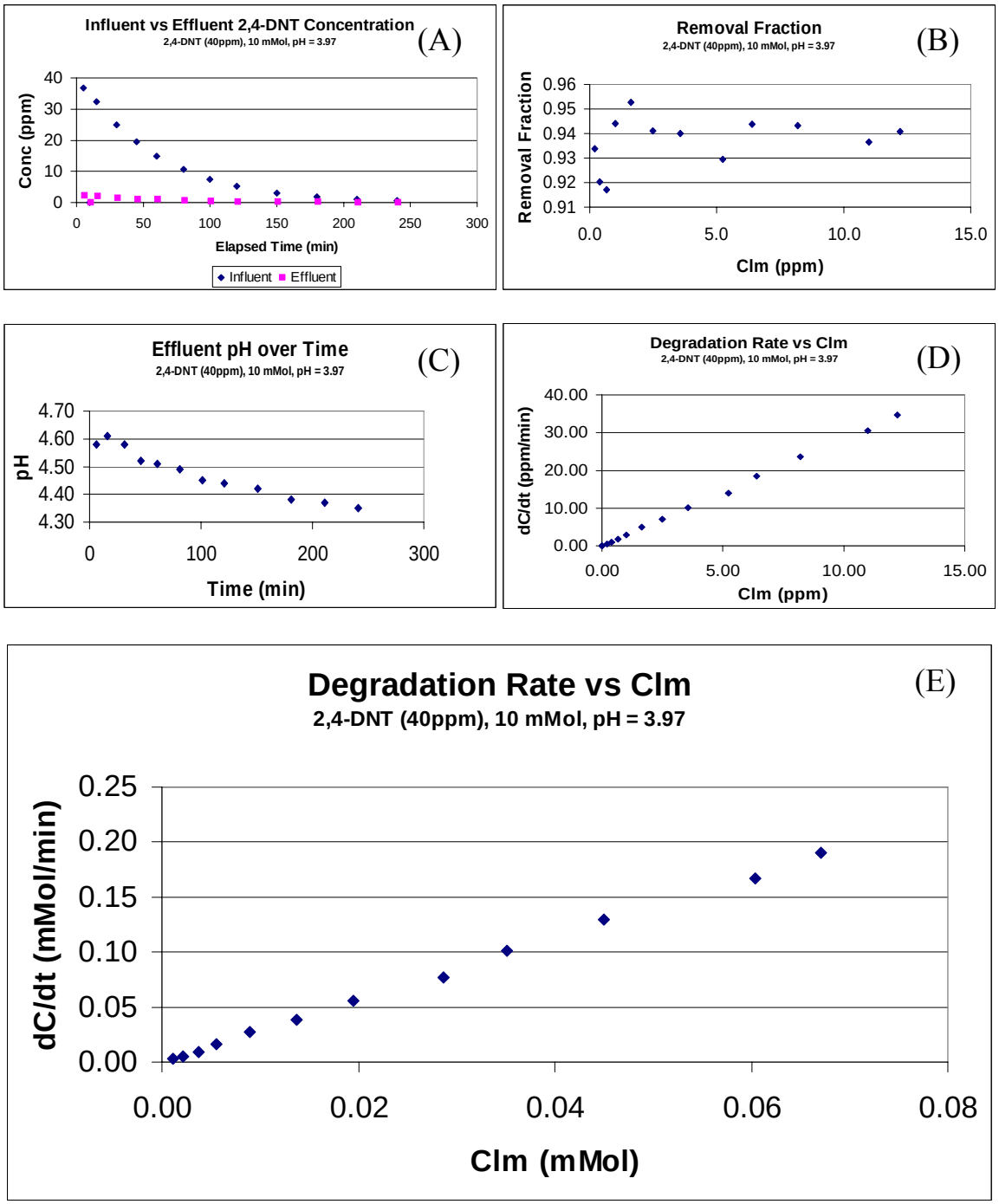
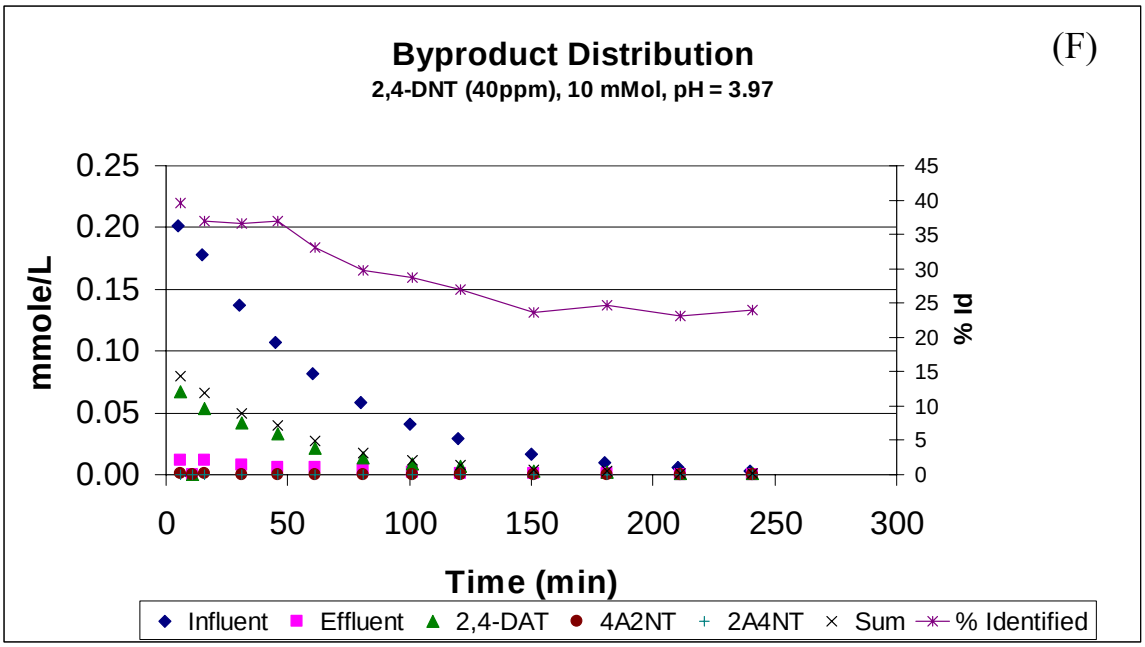


Figure A.18a Exp #18 – 40 ppm 2,4-DNT, 10mMol Formic acid, pH = 3.97 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



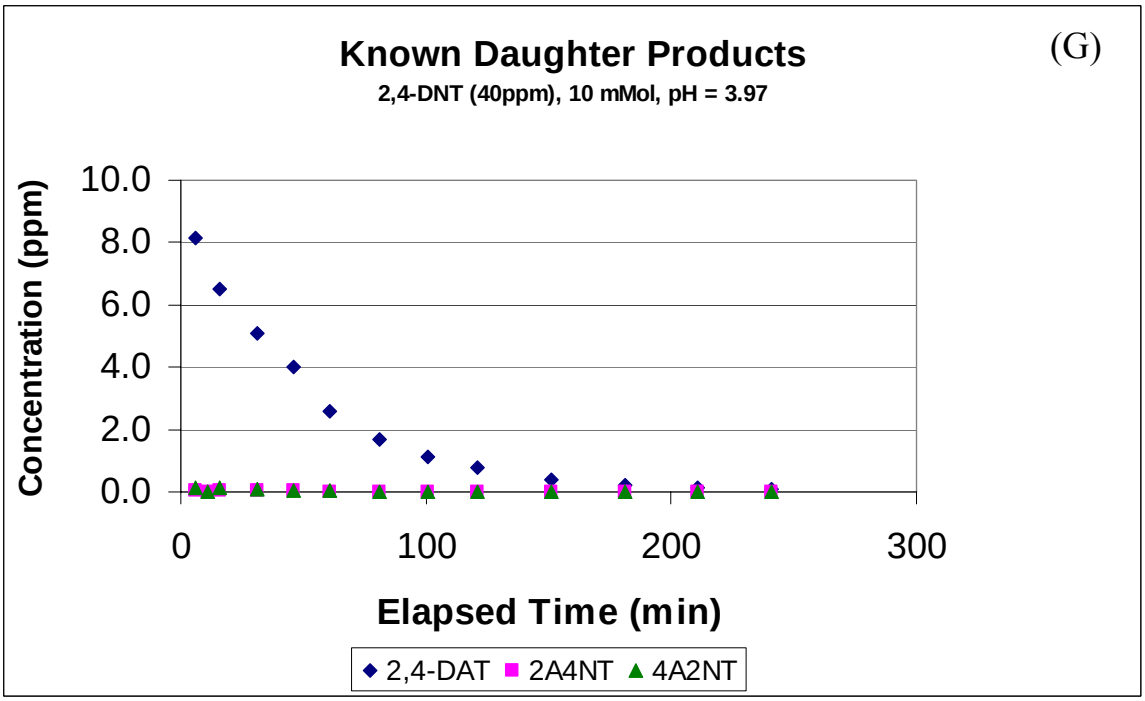


Figure A.18b Exp #18 – 40 ppm 2,4-DNT, 10mMol Formic acid, pH = 3.97 (F) Byproduct Distribution (G) Known Daughter Products

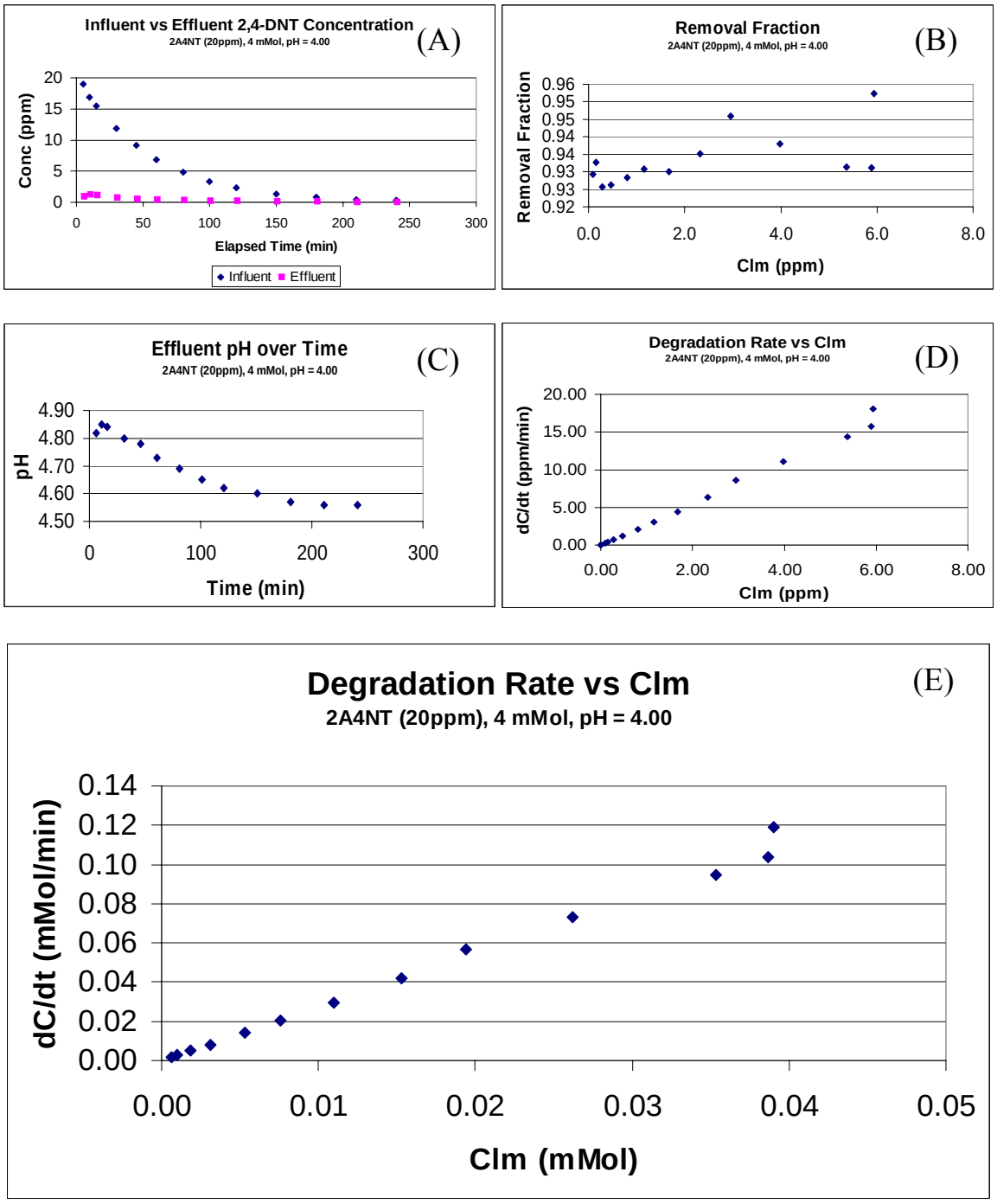
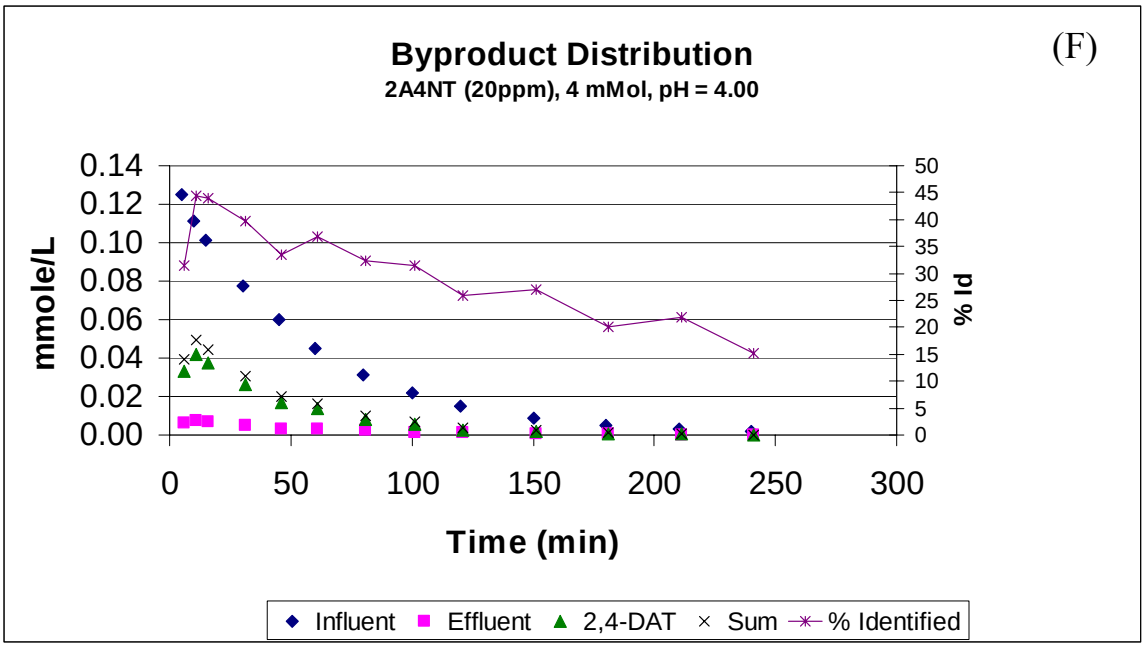


Figure A.19a Exp #19 – 20 ppm 2A4NT, 4mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2A4NT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



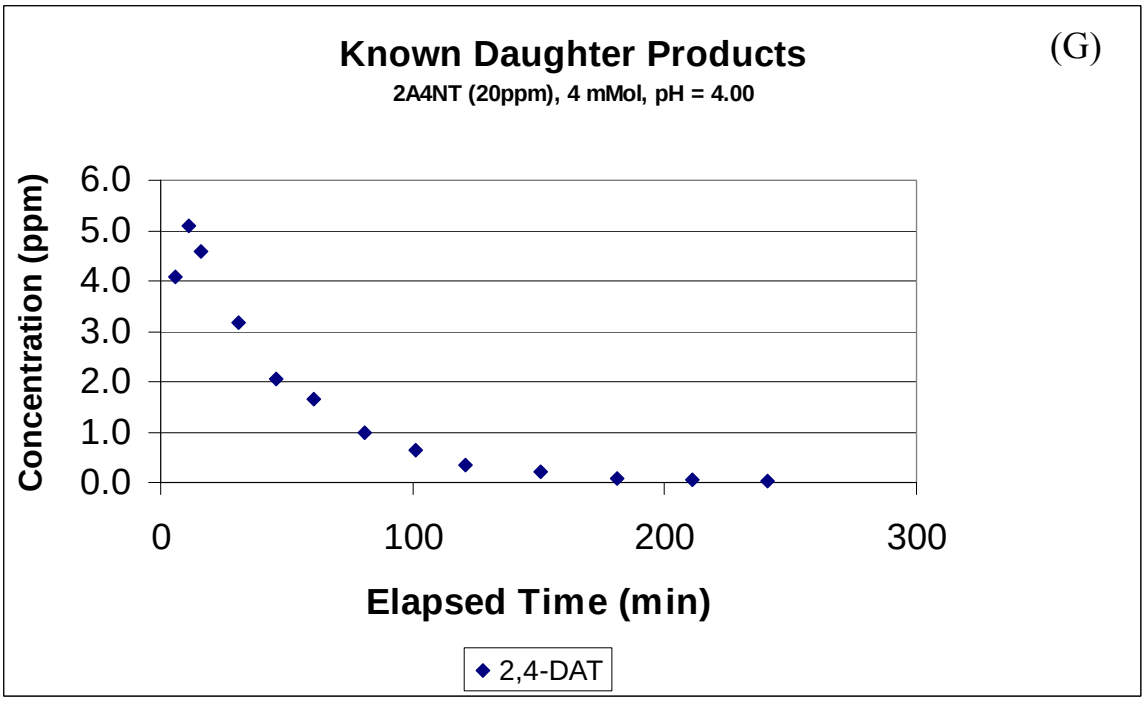


Figure A.19b Exp #19 – 20 ppm 2A4NT, 4mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

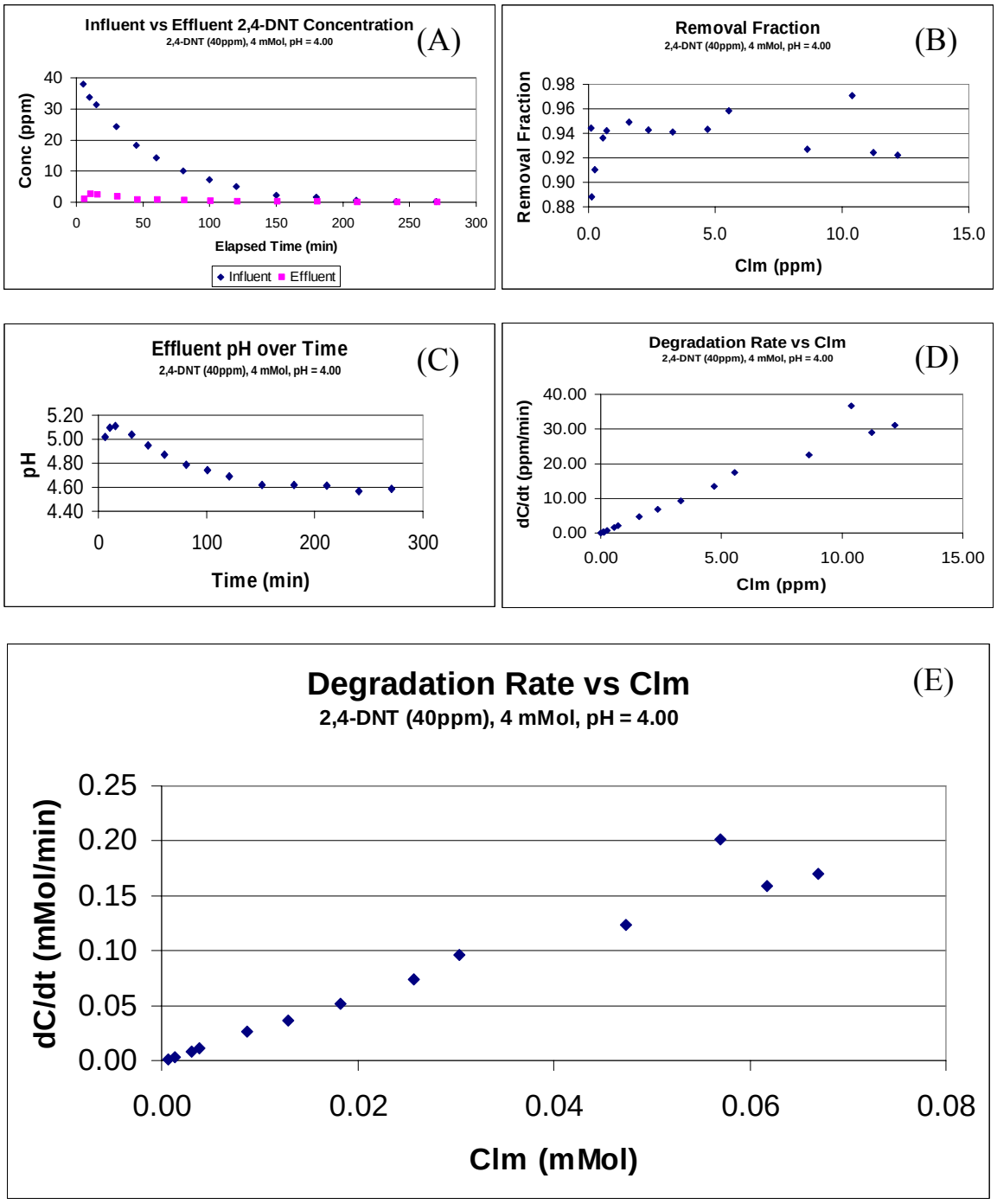
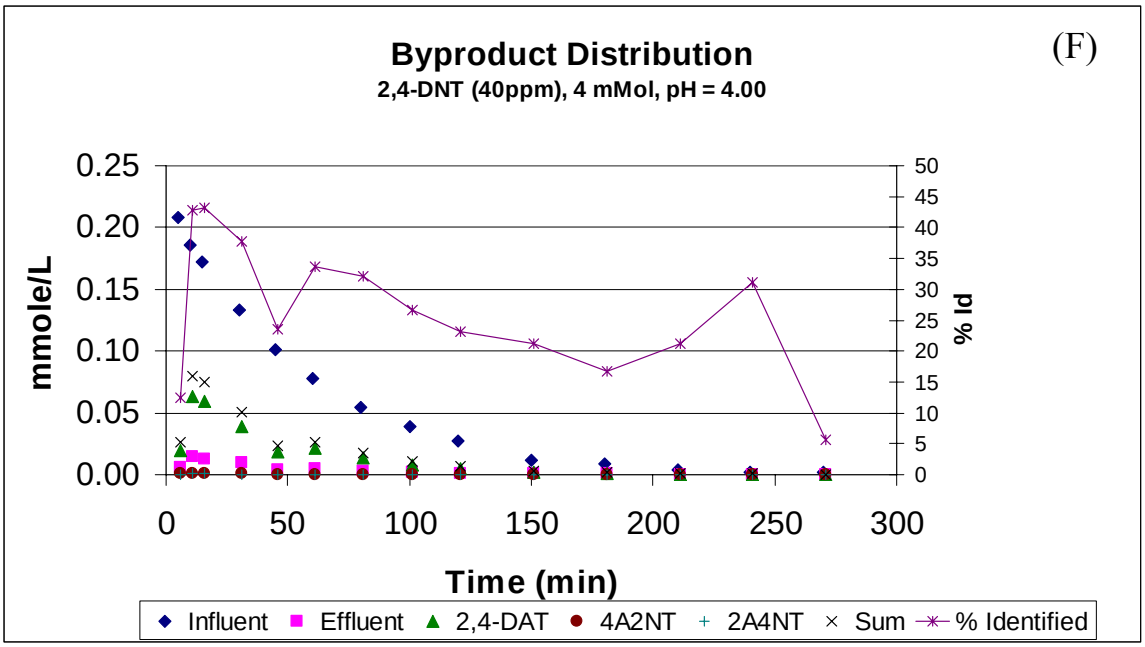


Figure A.20a Exp #20 – 40 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



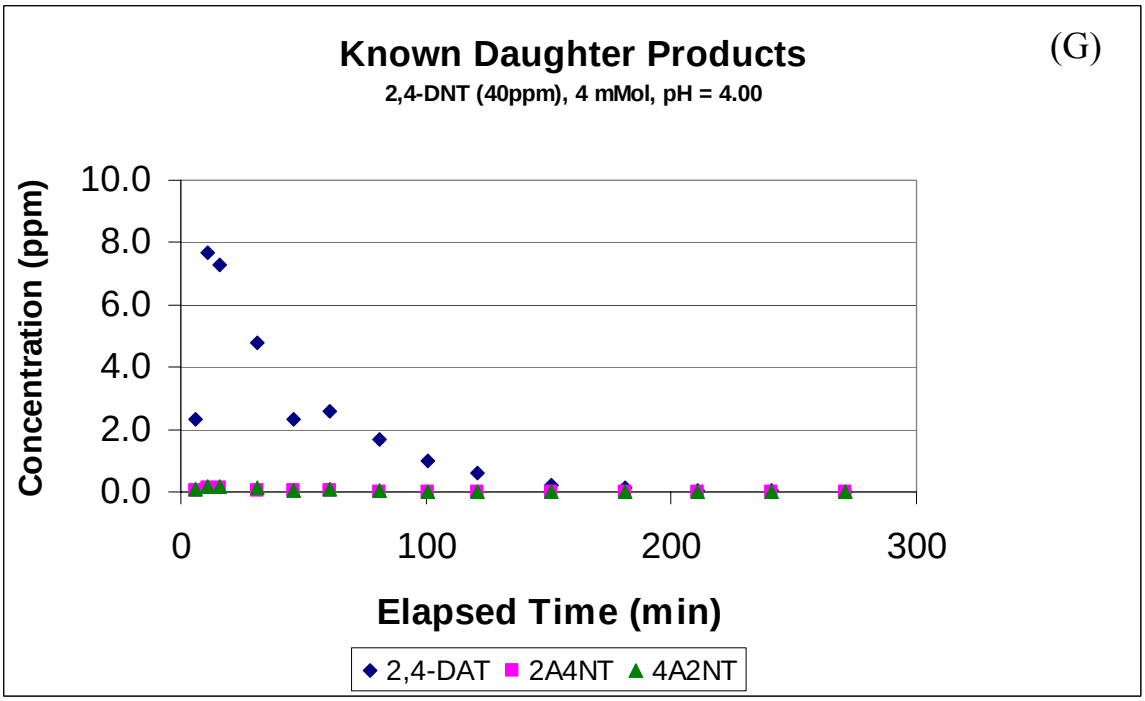


Figure A.20b Exp #20 – 40 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

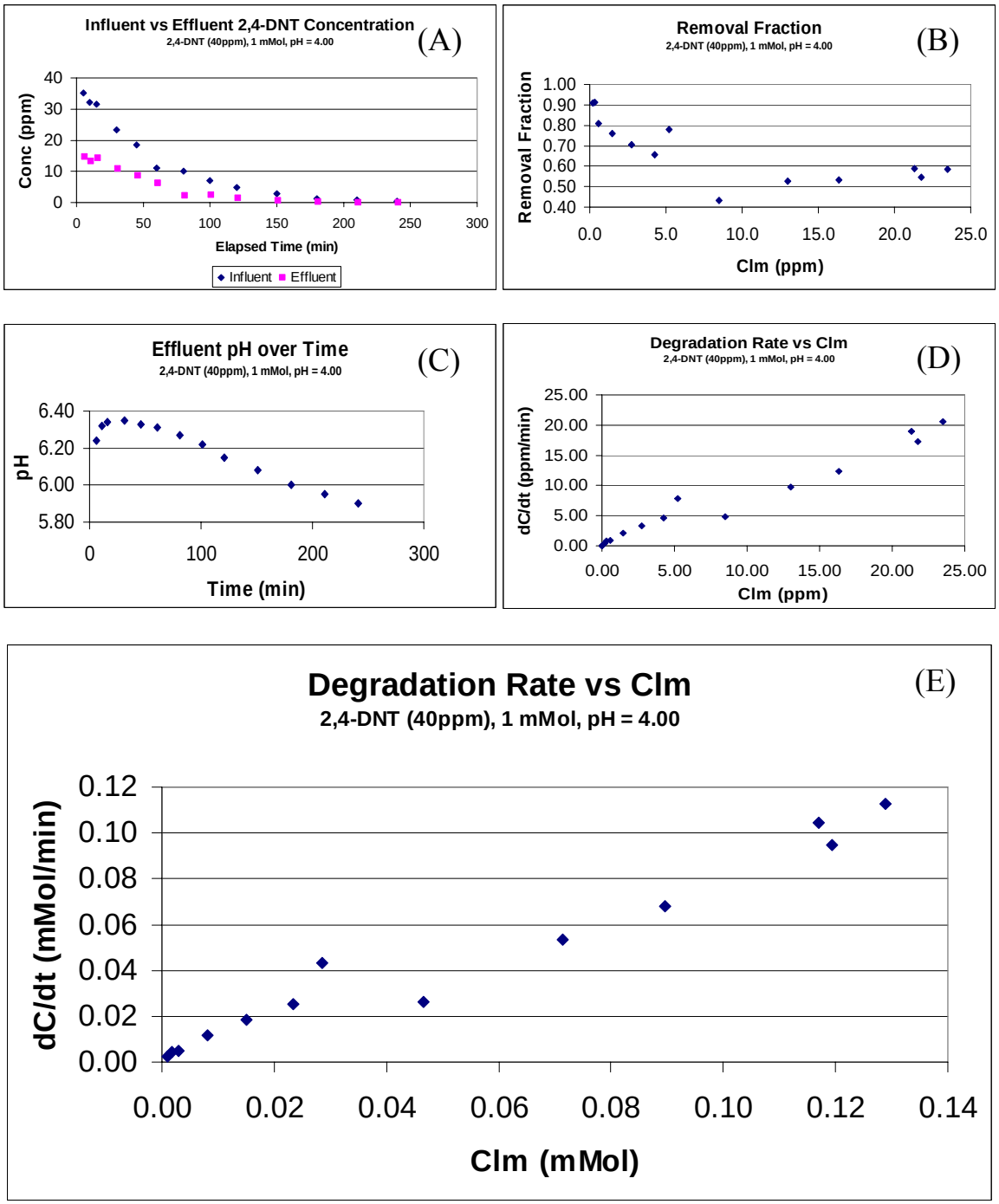
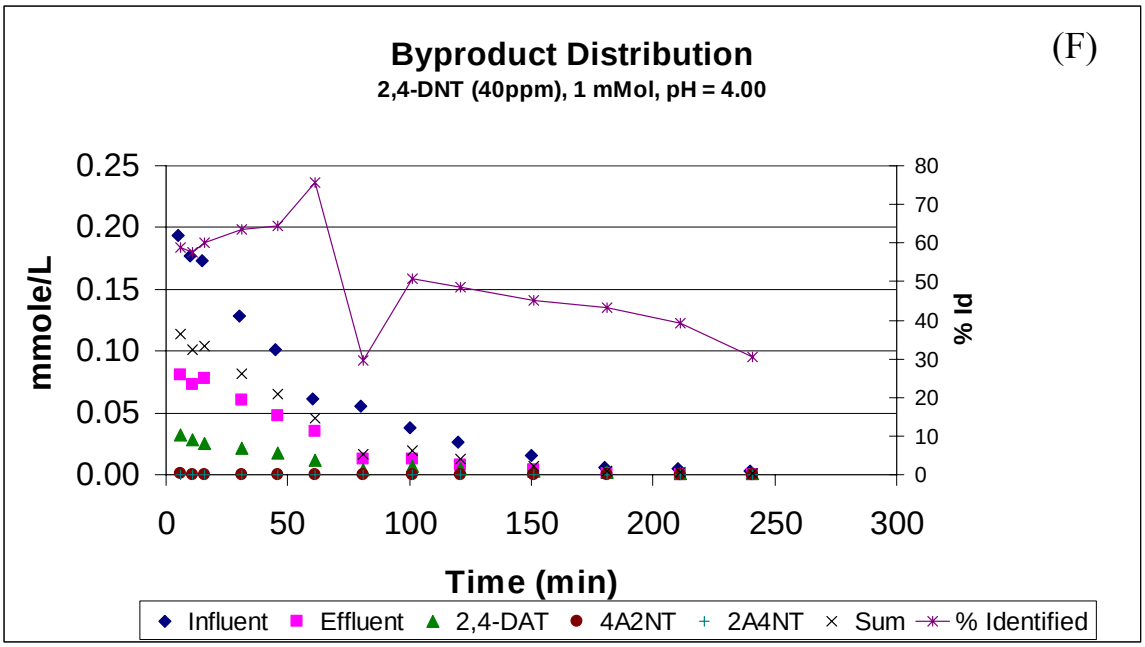


Figure A.21a Exp #21 – 40 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



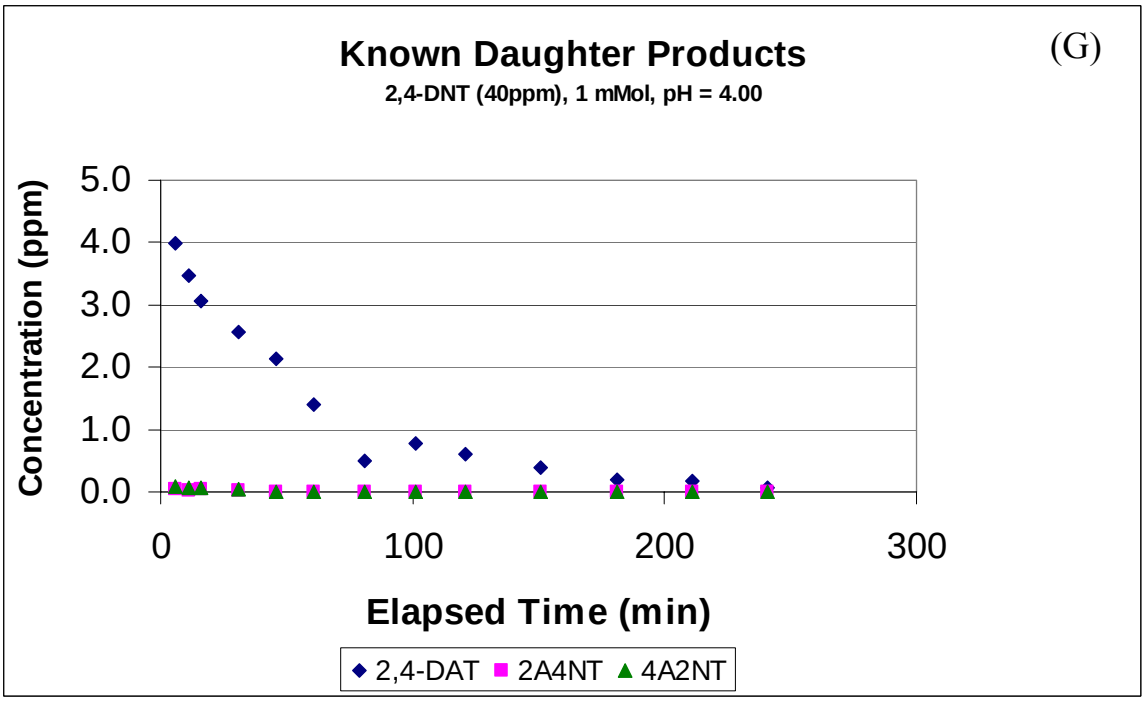


Figure A.21b Exp #21 – 40 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

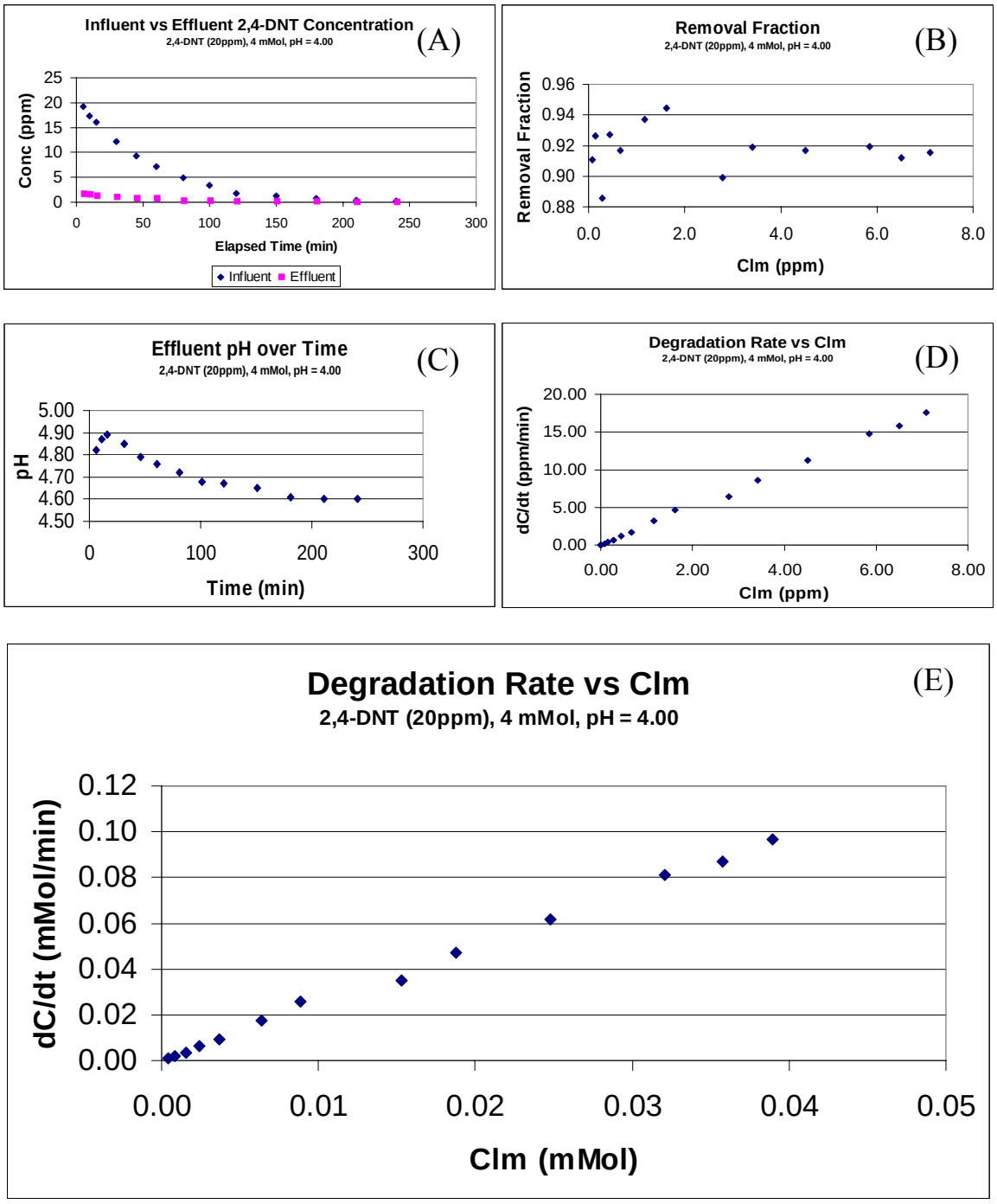
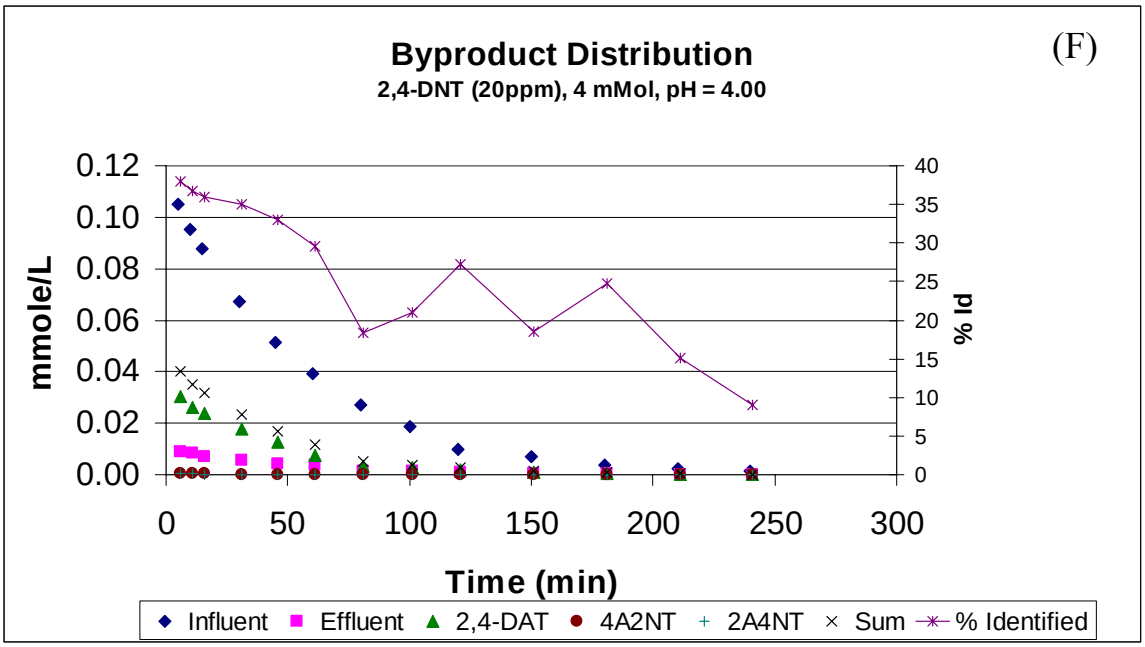


Figure A.22a Exp #22 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



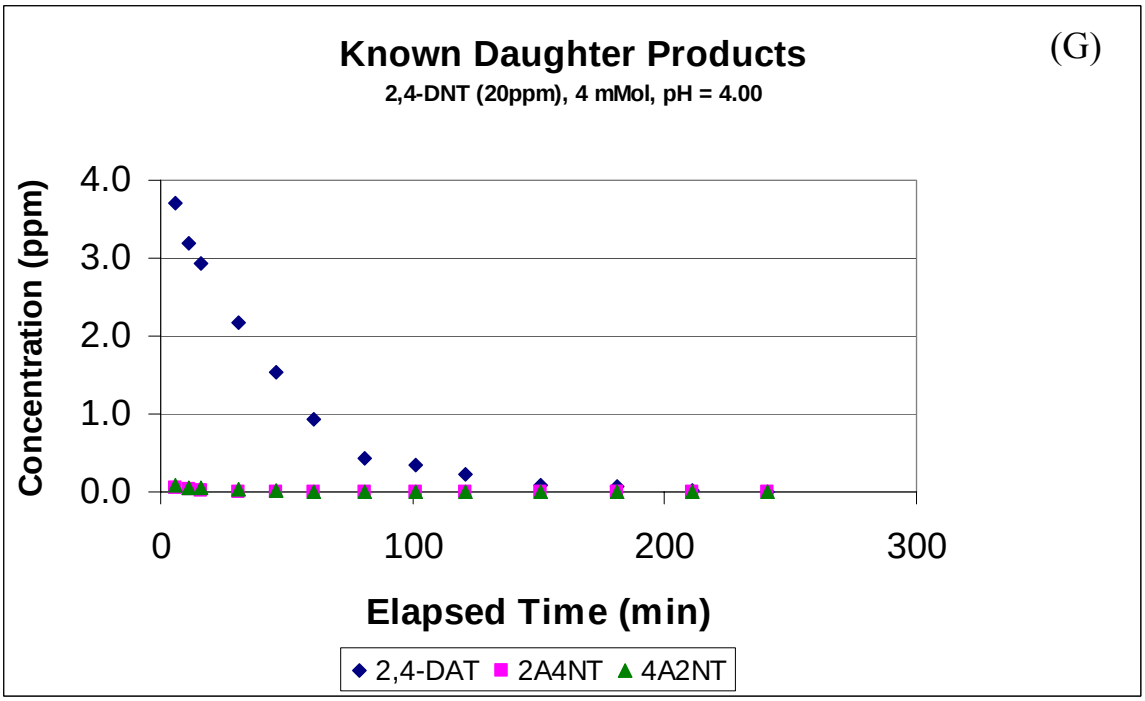


Figure A.22b Exp #22 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

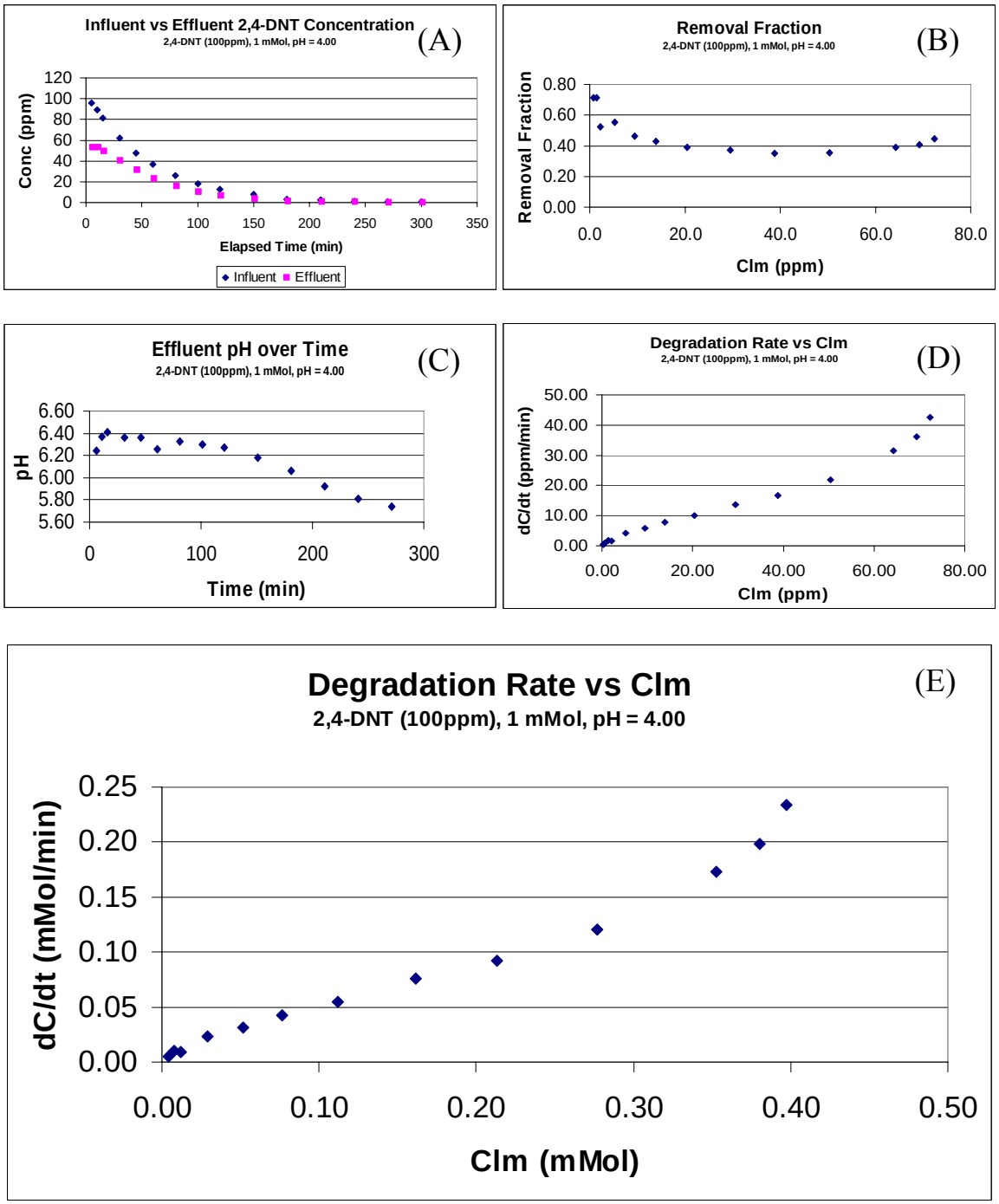
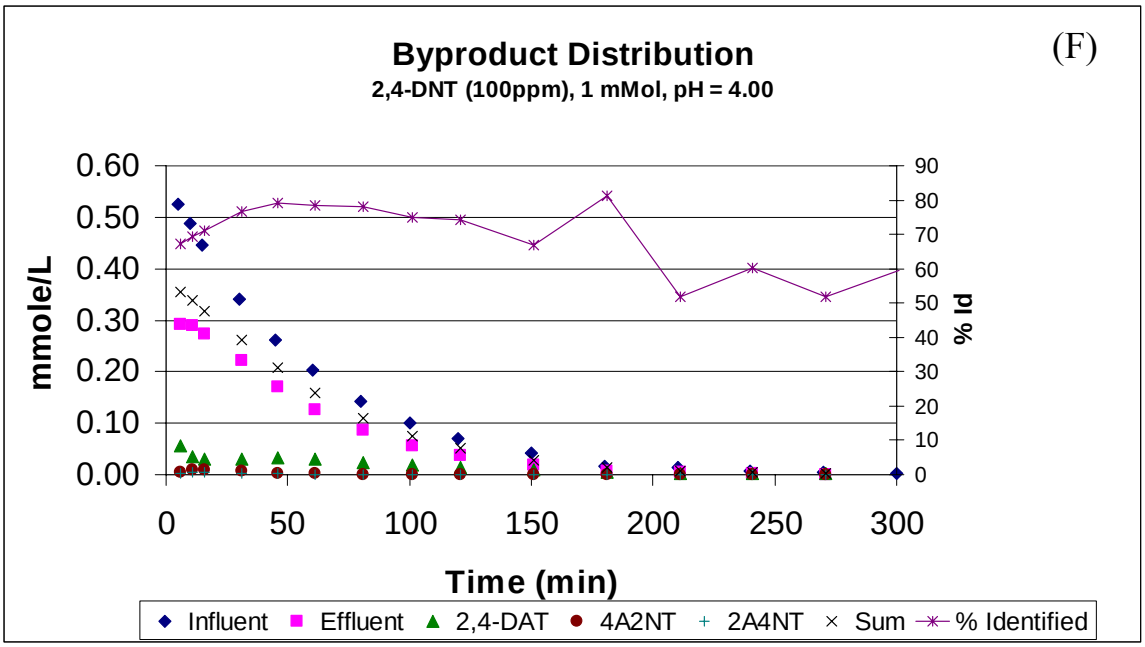


Figure A.23a Exp #23 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



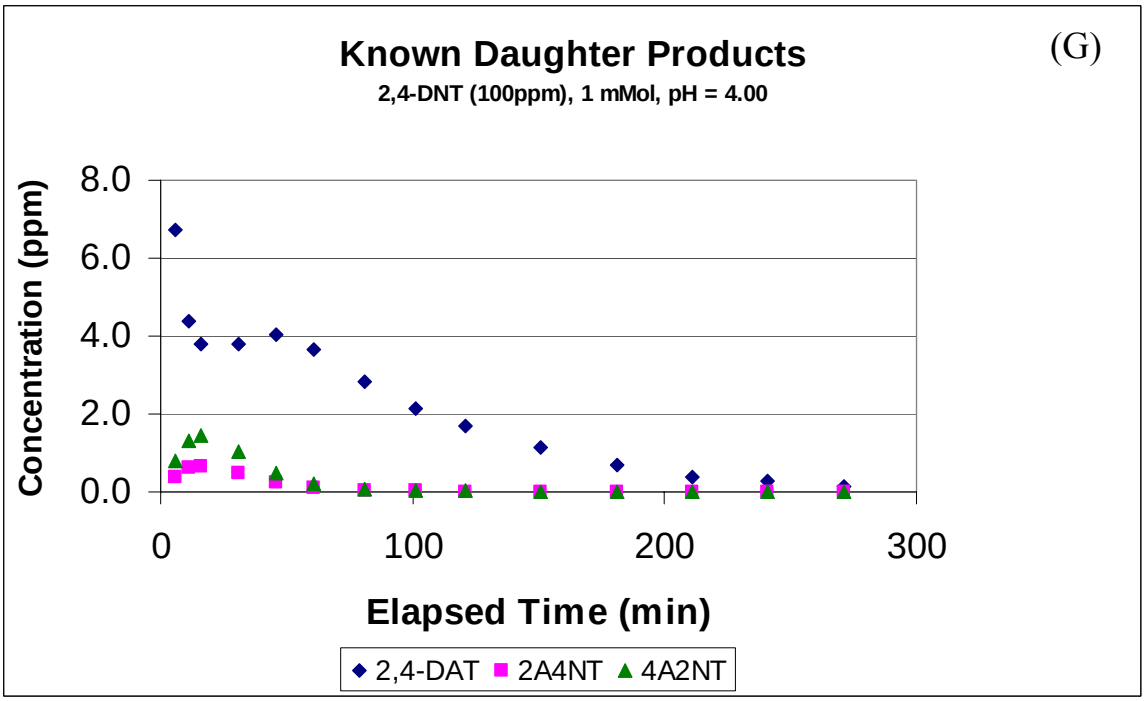


Figure A.23b Exp #23 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 (F) Byproduct Distribution (G) Known Daughter Products

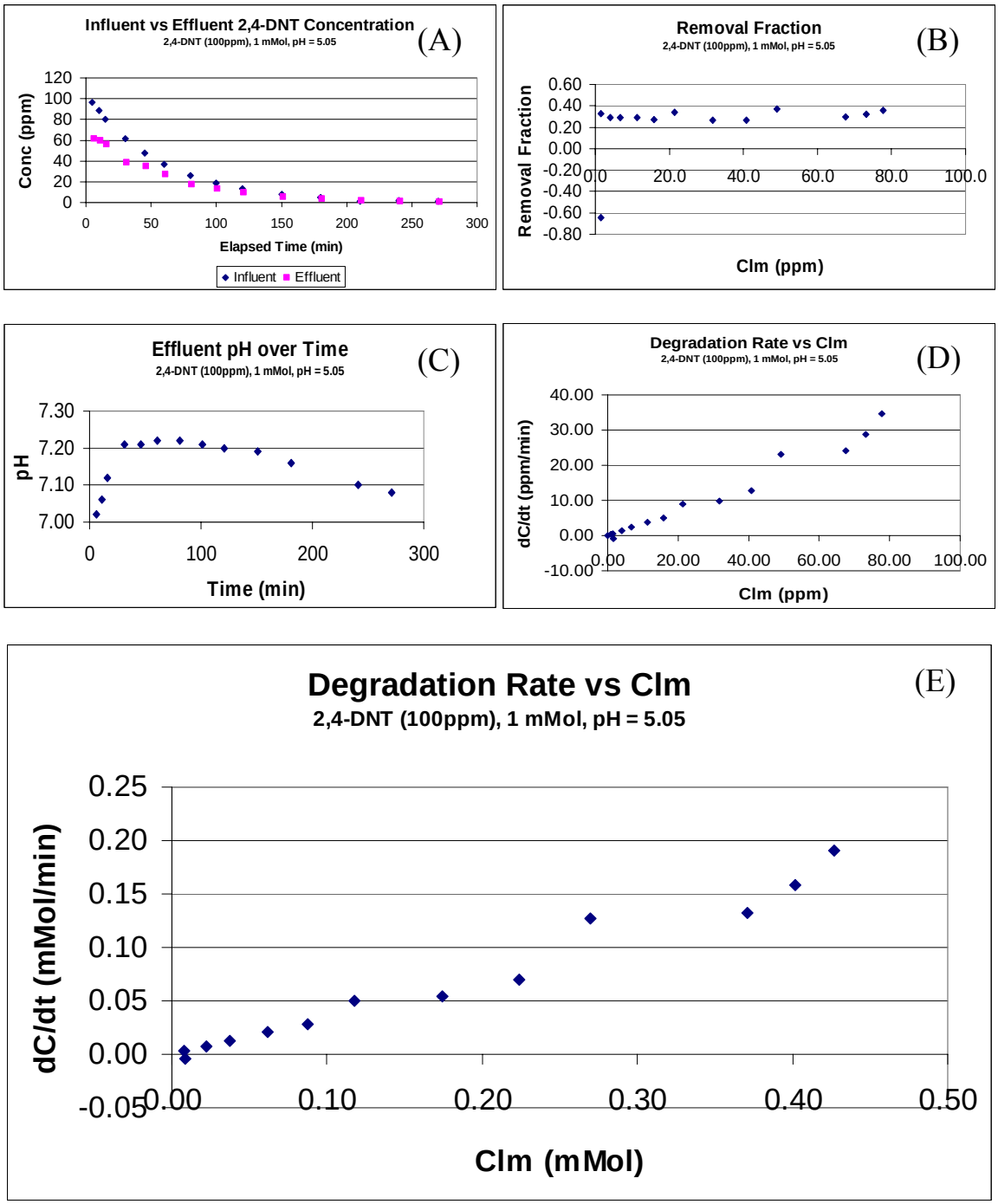
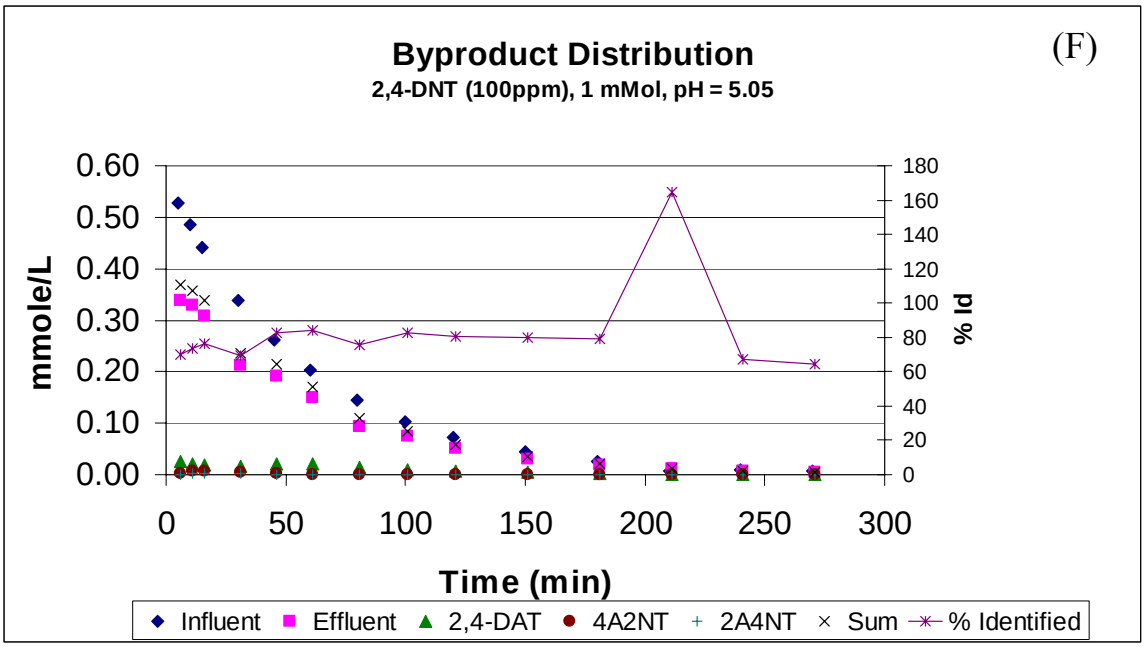


Figure A.24a Exp #24 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 5.05 (A) Influent vs. Effluent 2,4-DNT Concentration (B) Removal vs. Clm (ppm) (C) Effluent pH vs. Time (D) Degradation Rate vs. Clm (ppm) (E) Degradation Rate vs. Clm (mMol)



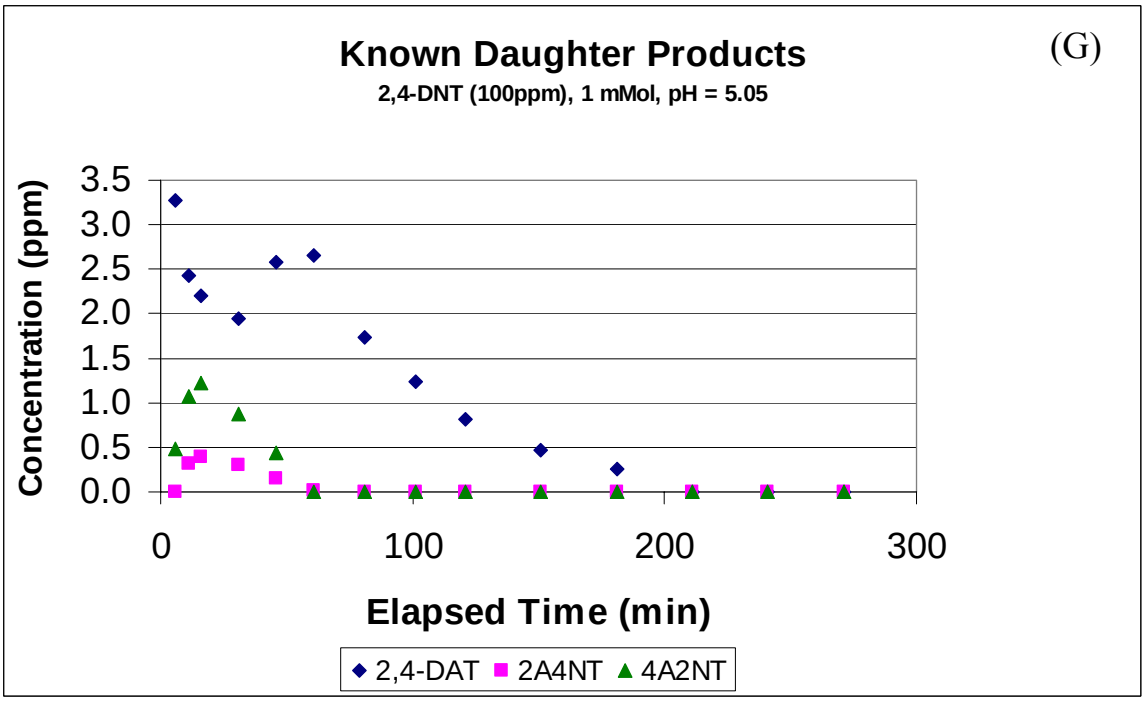


Figure A.24b Exp #24 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 5.05 (F) Byproduct Distribution (G) Known Daughter Products

APPENDIX B

UNKNOWN BYPRODUCT RESULTS

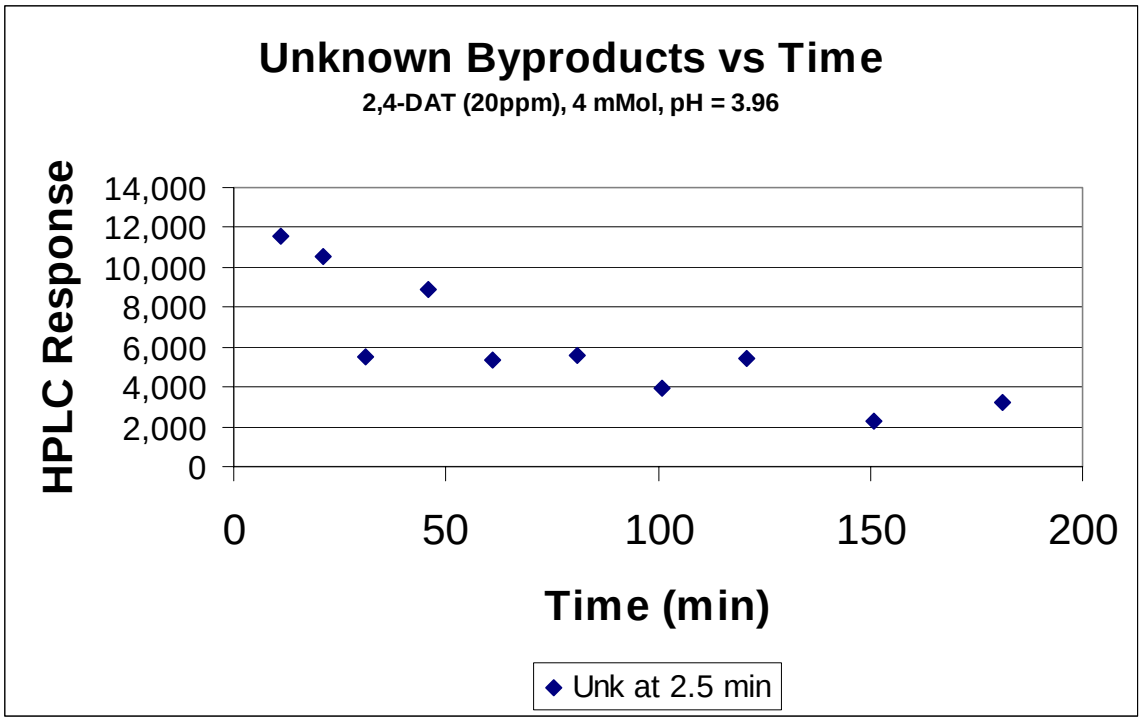


Figure B.1 Exp #9 – 20 ppm 2,4-DAT, 4mMol Formic acid, pH = 3.96 Unknown Byproducts at HPLC Time

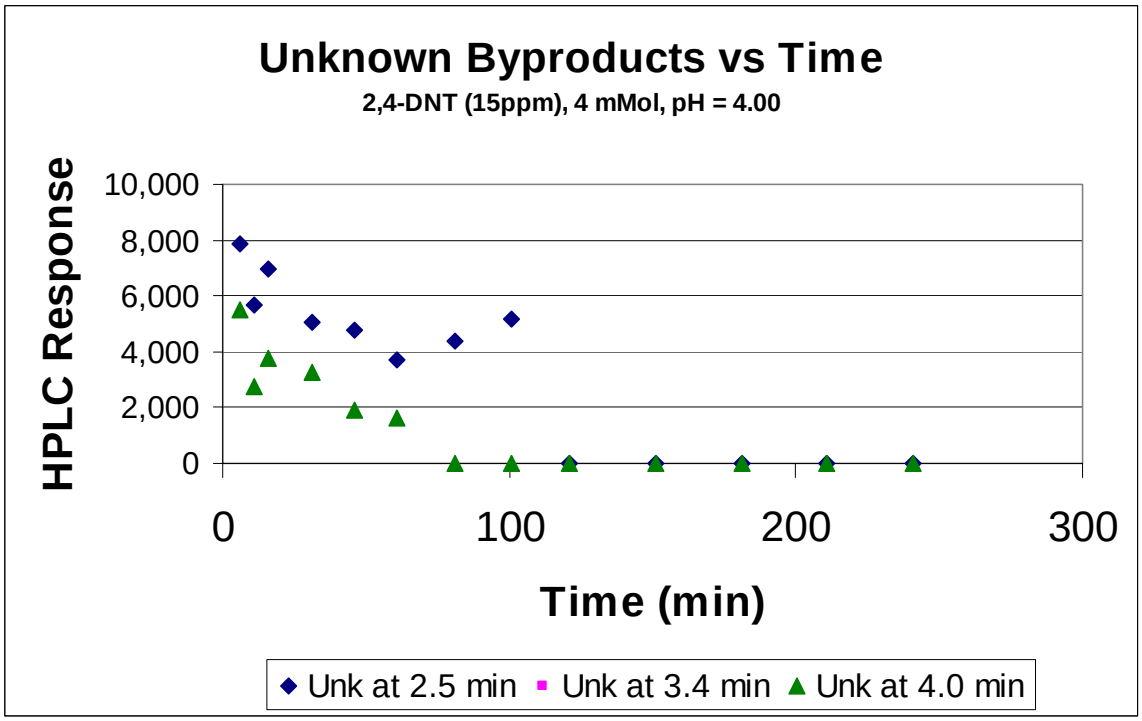


Figure B.2 Exp #12 – 15 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

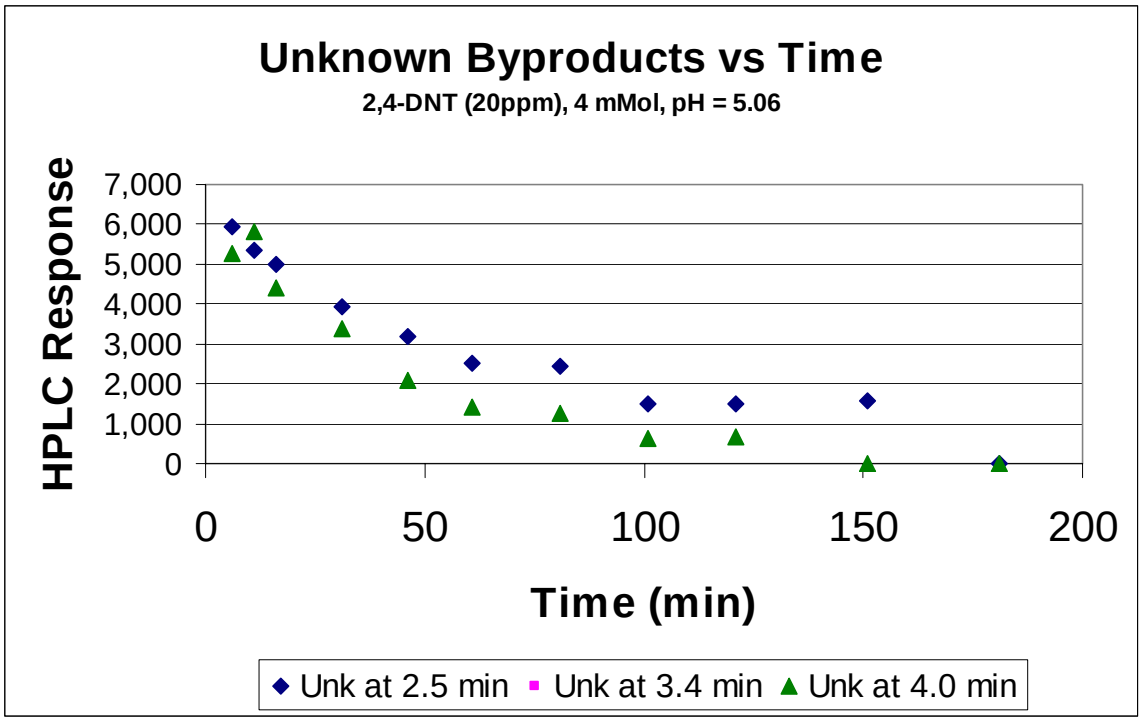


Figure B.3 Exp #13 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 5.06 Unknown Byproducts at HPLC Time

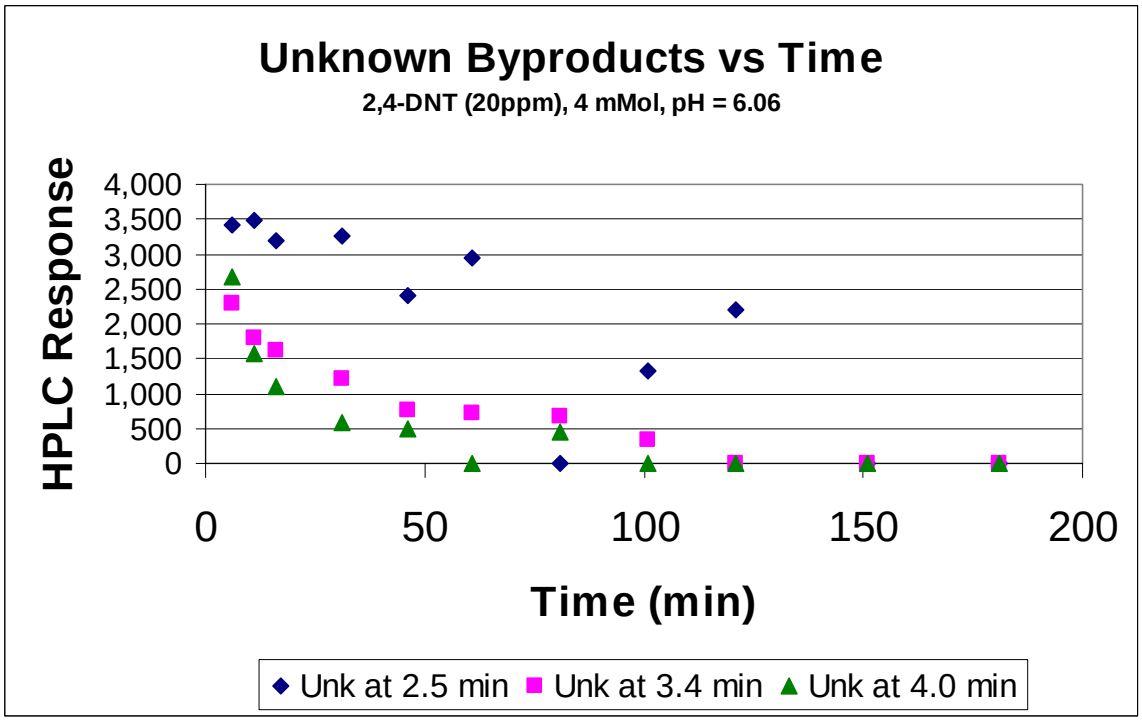


Figure B.4 Exp #14 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 6.06 Unknown Byproducts at HPLC Time

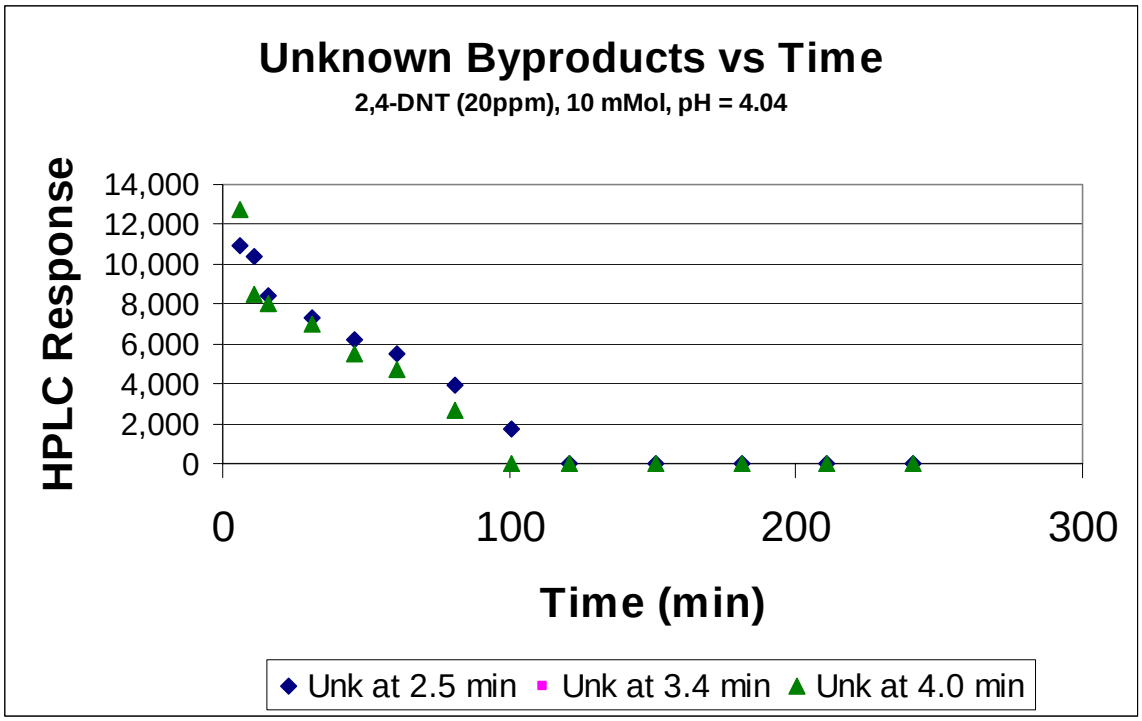


Figure B.5 Exp #15 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.04 Unknown Byproducts at HPLC Time

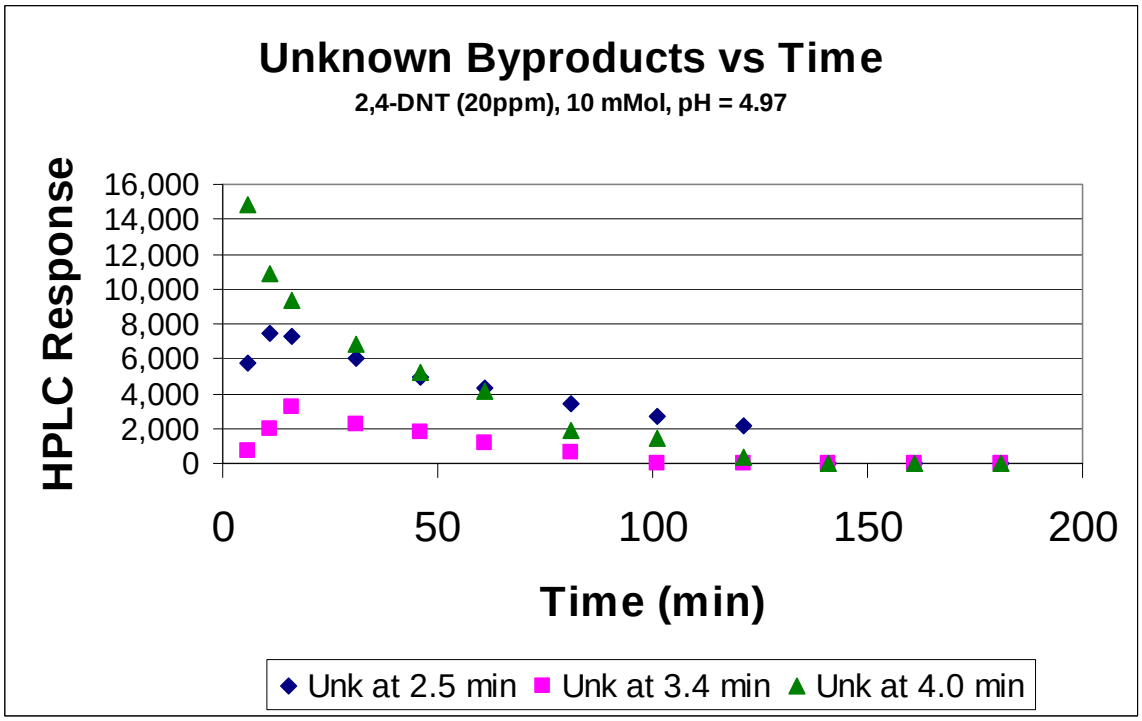


Figure B.6 Exp #16 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 4.97 Unknown Byproducts at HPLC Time

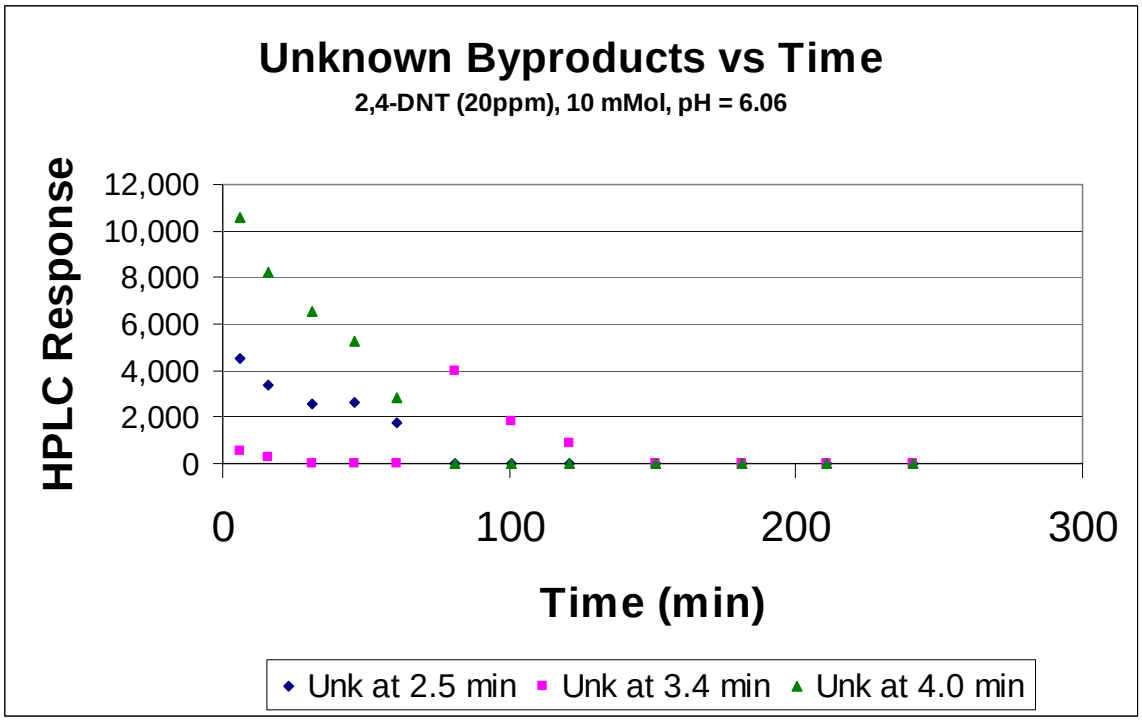


Figure B.7 Exp #17 – 20 ppm 2,4-DNT, 10mMol Formic acid, pH = 6.06 Unknown Byproducts at HPLC Time

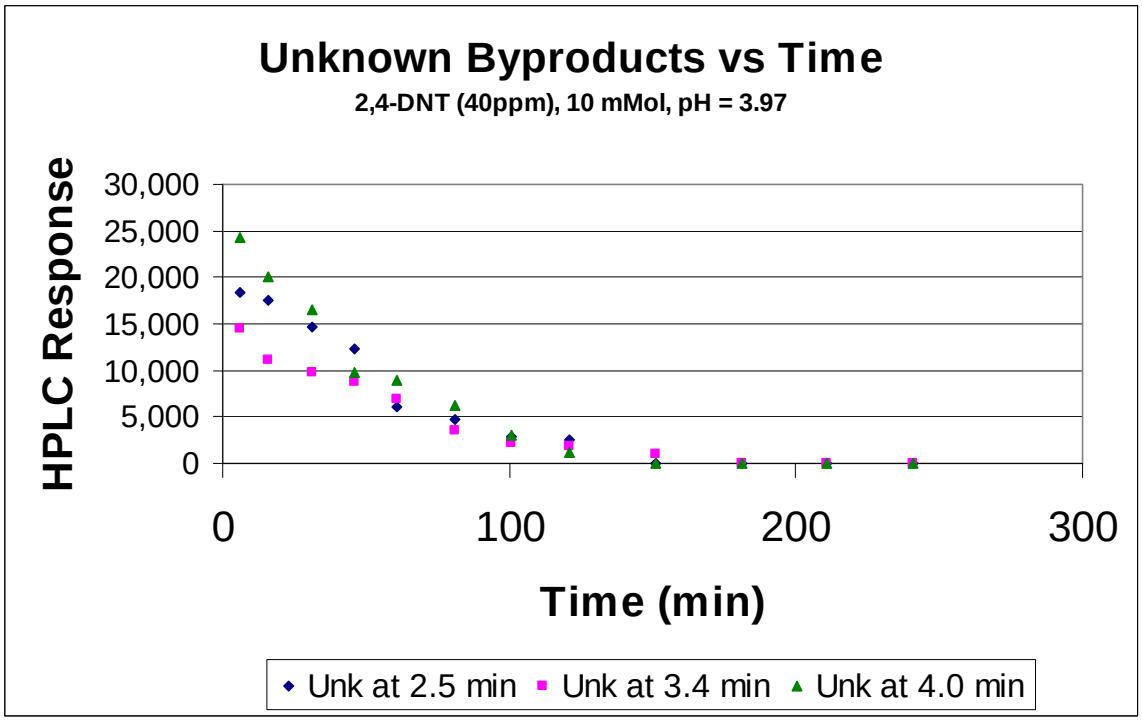


Figure B.8 Exp #18 – 40 ppm 2,4-DNT, 10mMol Formic acid, pH = 3.97 Unknown Byproducts at HPLC Time

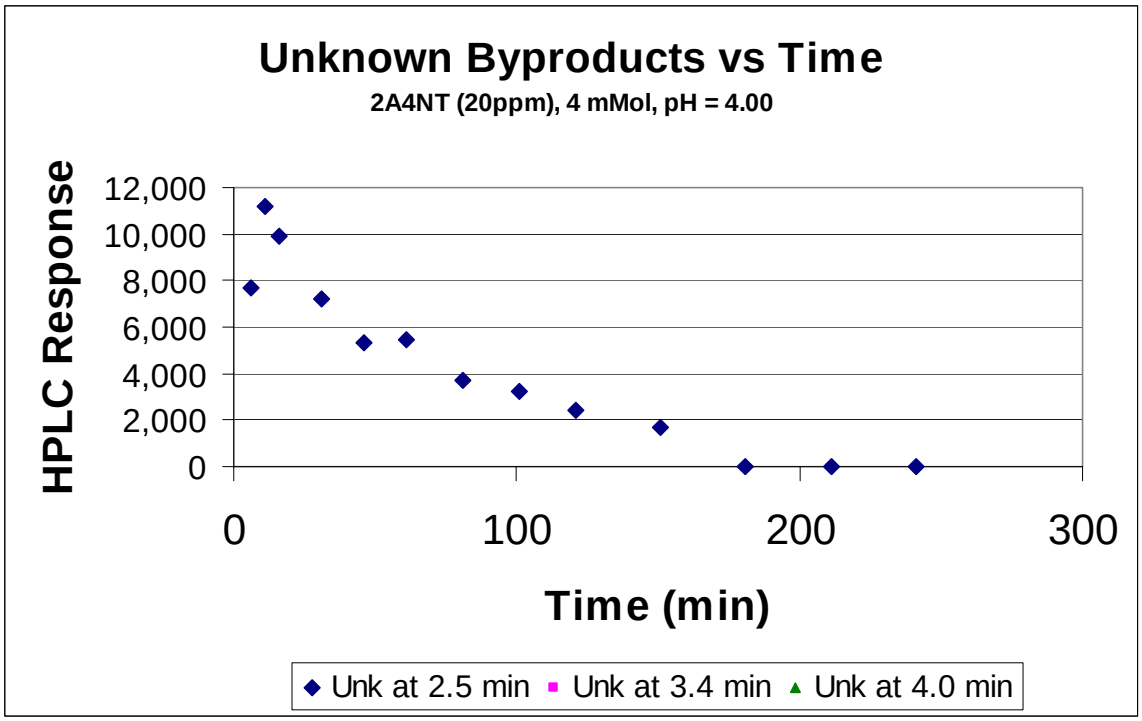


Figure B.9 Exp #19 – 20 ppm 2A4NT, 4mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

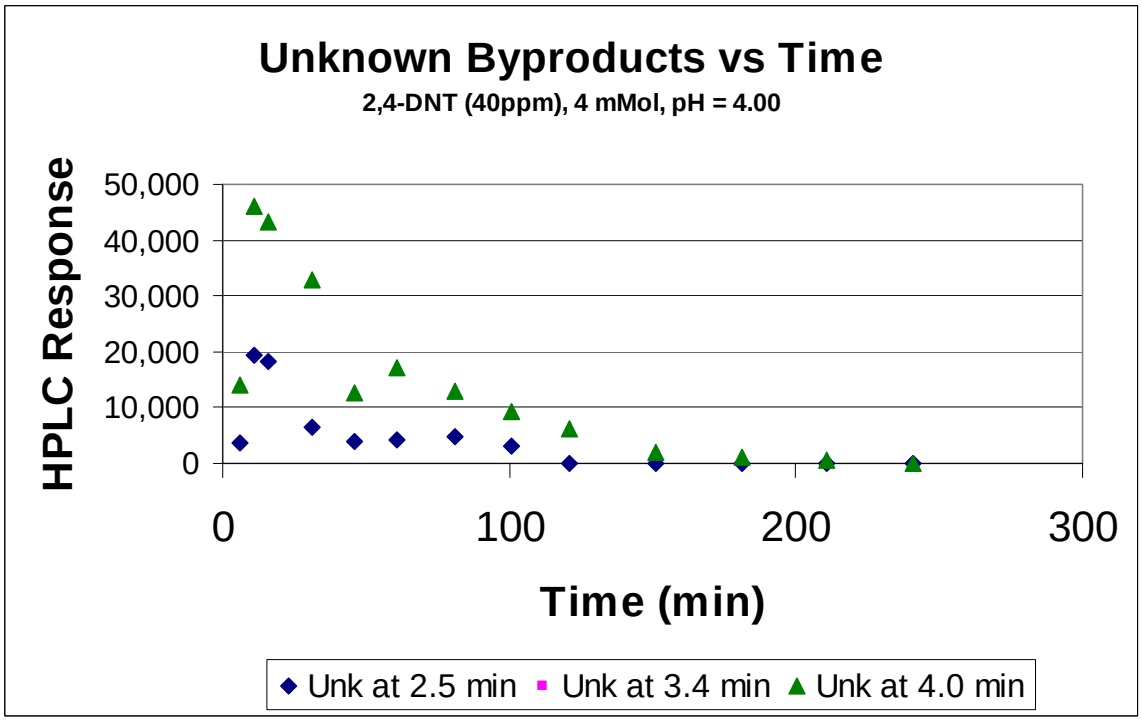


Figure B.10 Exp #20 – 40 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

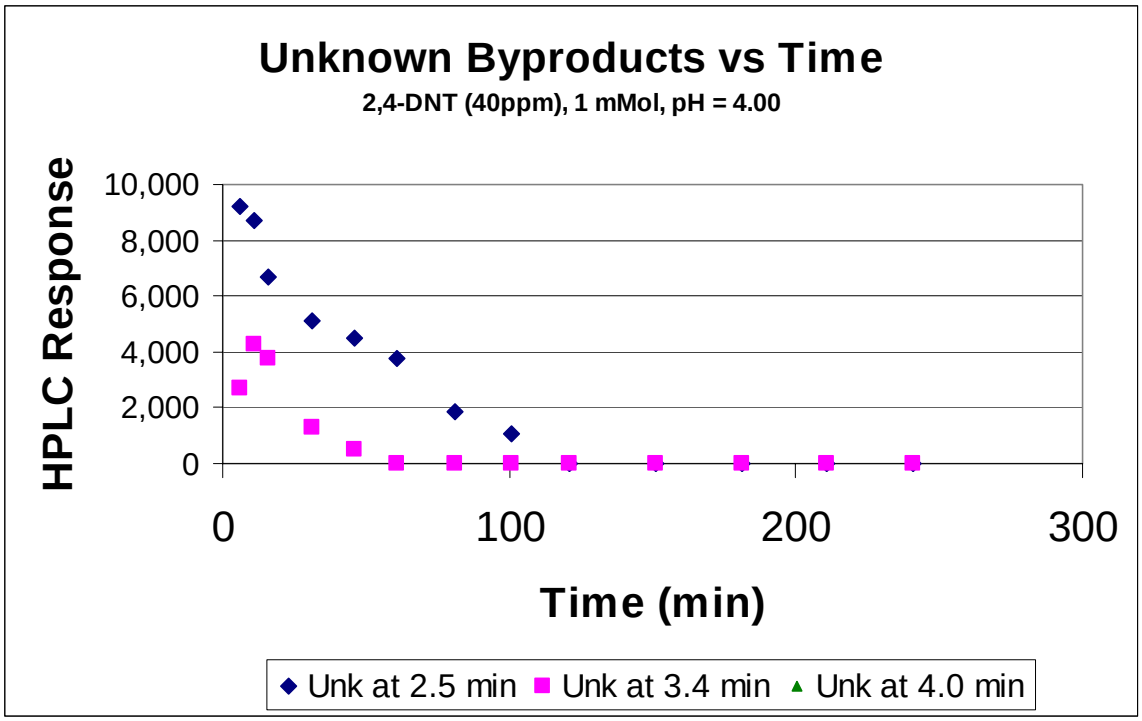


Figure B.11 Exp #21 – 40 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

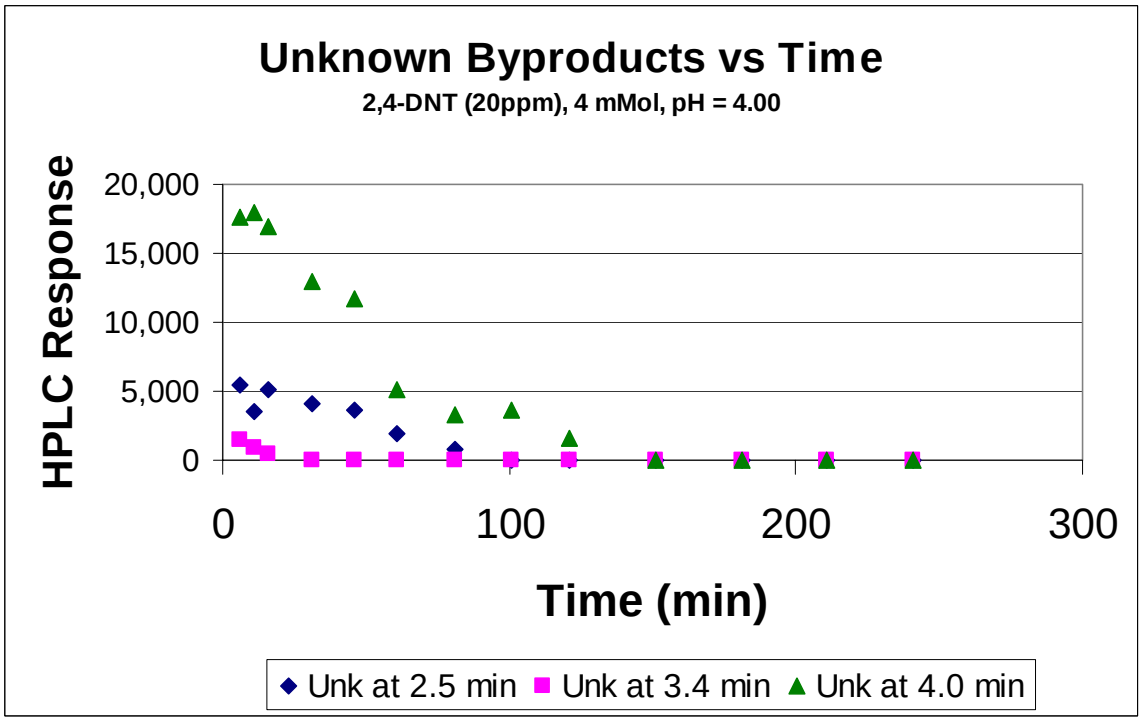


Figure B.12 Exp #22 – 20 ppm 2,4-DNT, 4mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

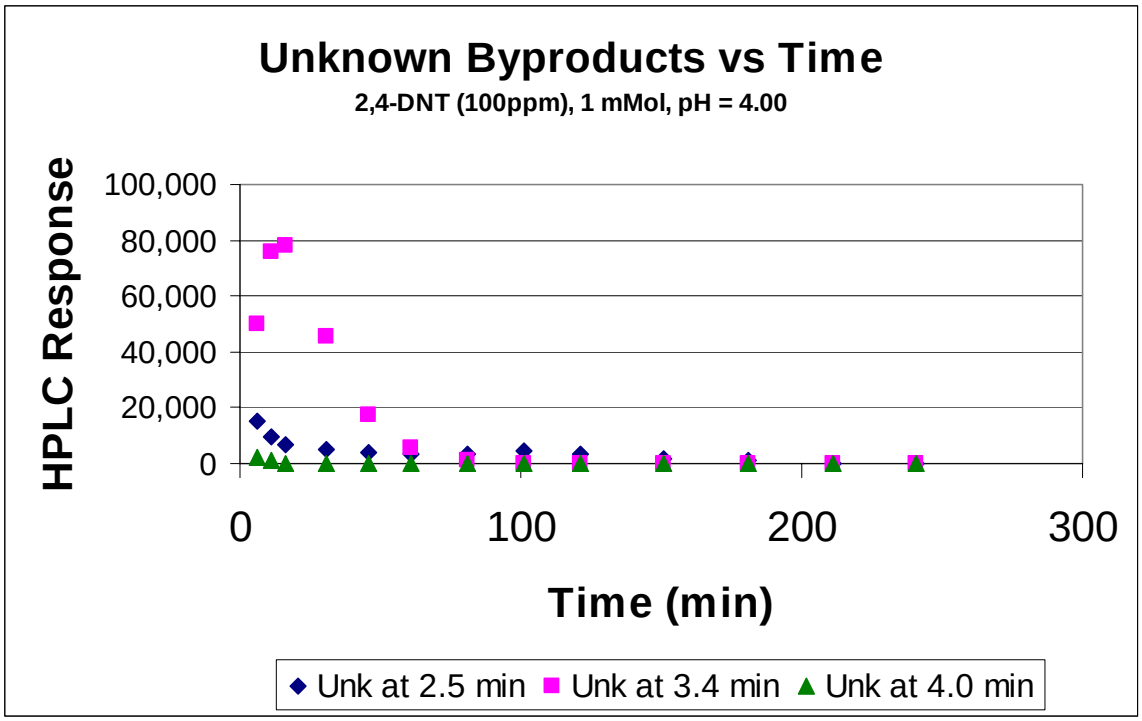


Figure B.13 Exp #23 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 4.00 Unknown Byproducts at HPLC Time

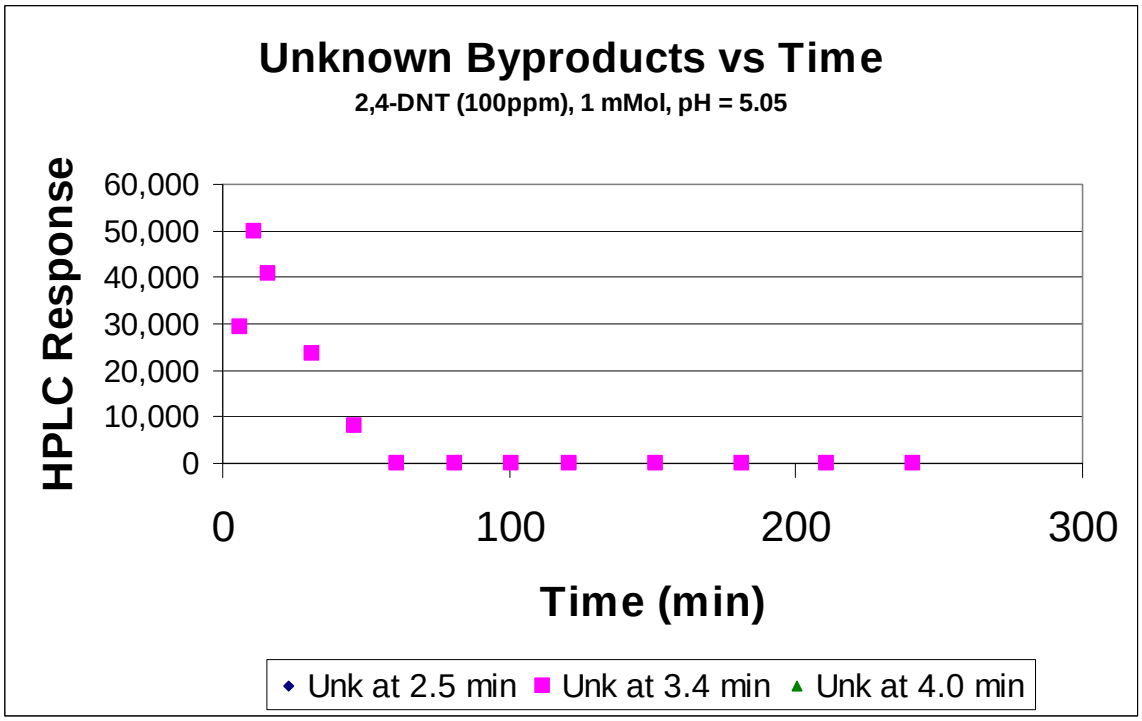


Figure B.14 Exp #24 – 100 ppm 2,4-DNT, 1mMol Formic acid, pH = 5.05 Unknown Byproducts at HPLC Time

APPENDIX C

CONTAMINANT HPLC STANDARDS

2,4-DNT

2,4-dinitrotoluene

Standard run through HPLC, 27 Oct 2003
2,4-DNT 2,4-dinitrotoluene

Time	Concentration (ppm)	Area
7.073	100	6,434,427
7.020	20	1,301,925
6.955	10	620,500
7.058	2	119,487

Table C.1 HPLC Data for 2,4-DNT Standard

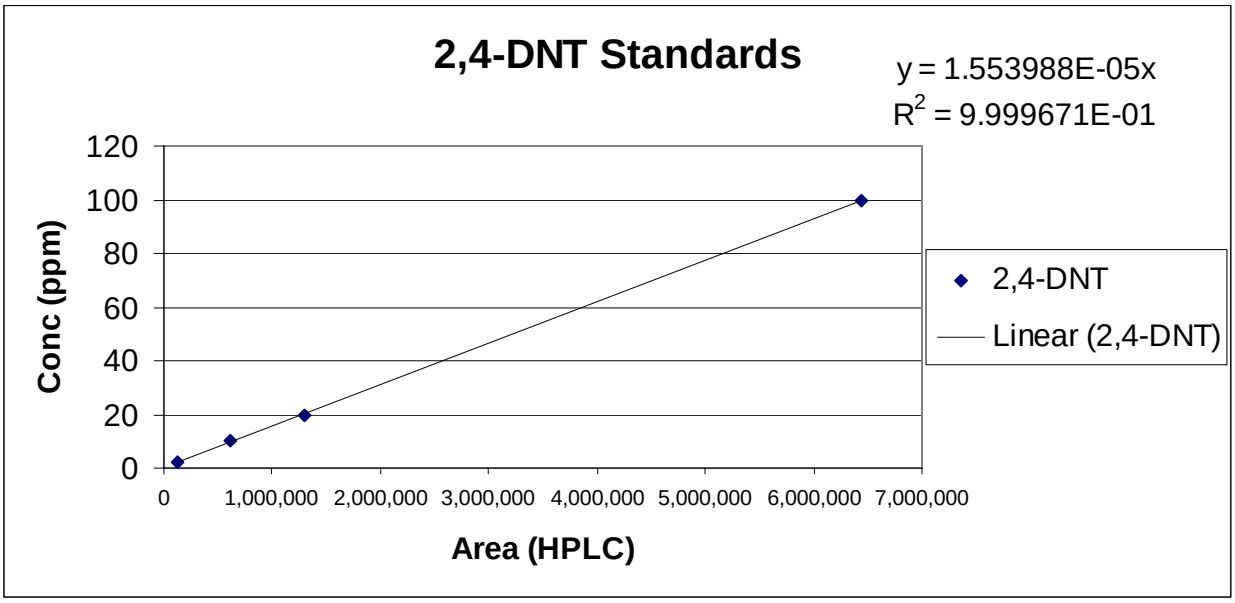


Figure C.1 HPLC Standard Curve with Linear Regression for 2,4-DNT.

2A4NT

2-amino-4-nitrotoluene

Standard run through HPLC, 12 Oct 2003

2A4NT 2-amino-4-nitrotoluene

Time	Concentration (ppm)	Area
5.095	200	11,333,782
5.043	50	2,953,070
5.043	20	1,131,039
5.068	10	566,035
5.070	2	136,530

Supplemental test 11 Nov 03

Time	Concentration (ppm)	Area
5.003	10	544,595

Table C.2 HPLC Data for 2A4NT Standard

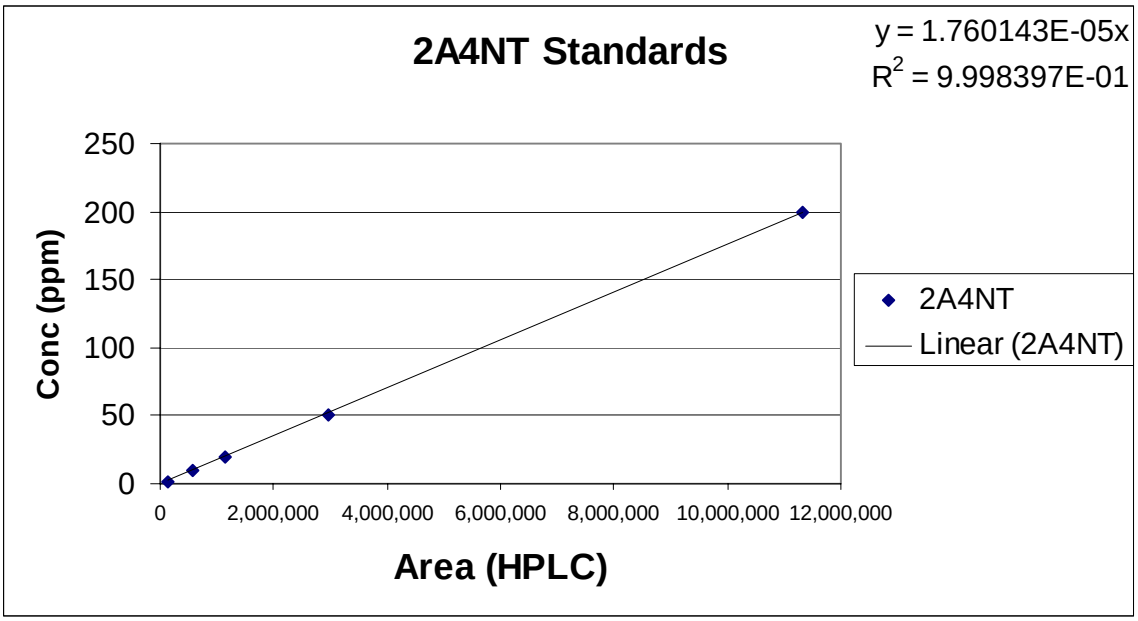


Figure C.2 HPLC Standard Curve with Linear Regression for 2A4NT.

4A2NT

4-amino-2-nitrotoluene

Standard run through HPLC, 11 Oct 2003
4A2NT 4-amino-2-nitrotoluene

Time	Concentration (ppm)	Area
4.873	100	4,119,884
4.856	50	2,106,079
4.846	20	842,316
4.856	10	424,607
4.863	2	89,164

Supplemental test 11 Nov 03

Time	Concentration (ppm)	Area
4.763	10	407,847

Table C.3 HPLC Data for 4A2NT Standard

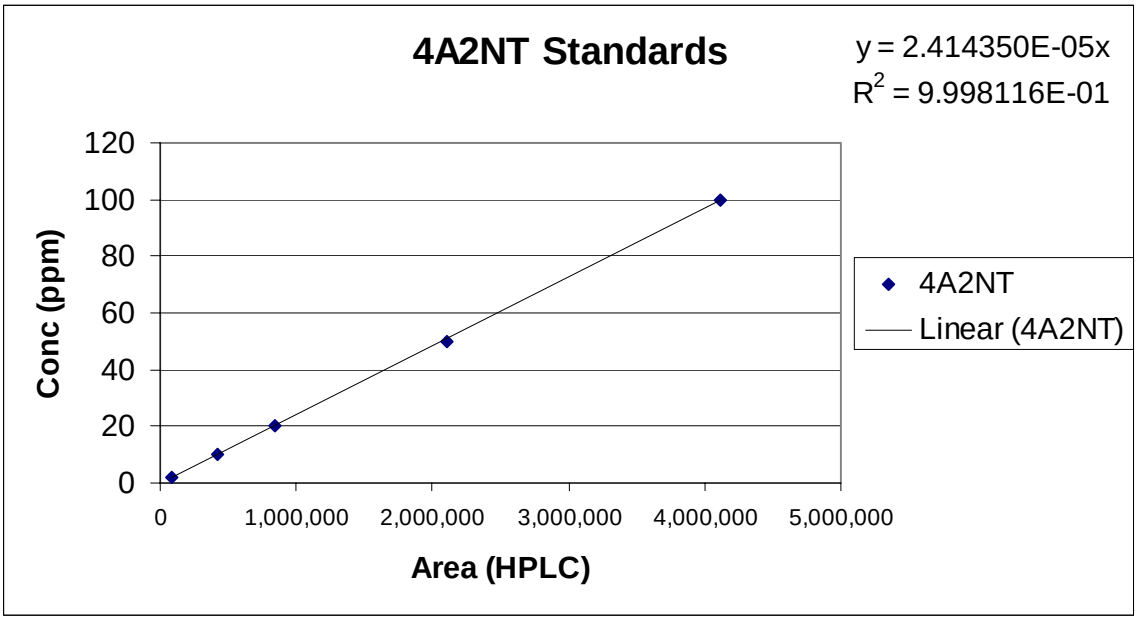


Figure C.3 HPLC Standard Curve with Linear Regression for 4A2NT.

2,4-DAT

2,4-diaminotoluene

Standards run through HPLC, 18 Aug 2003
2,4-DAT 2,4-diaminotoluene

Time	Concentration (ppm)	Area
2.885	100	2,016,086
2.878	50	1,012,239
2.898	20	412,079
2.893	10	199,975
2.873	2	48,870
2.891	2	38,008

Table C.4 HPLC Data for 2,4-DAT Standard

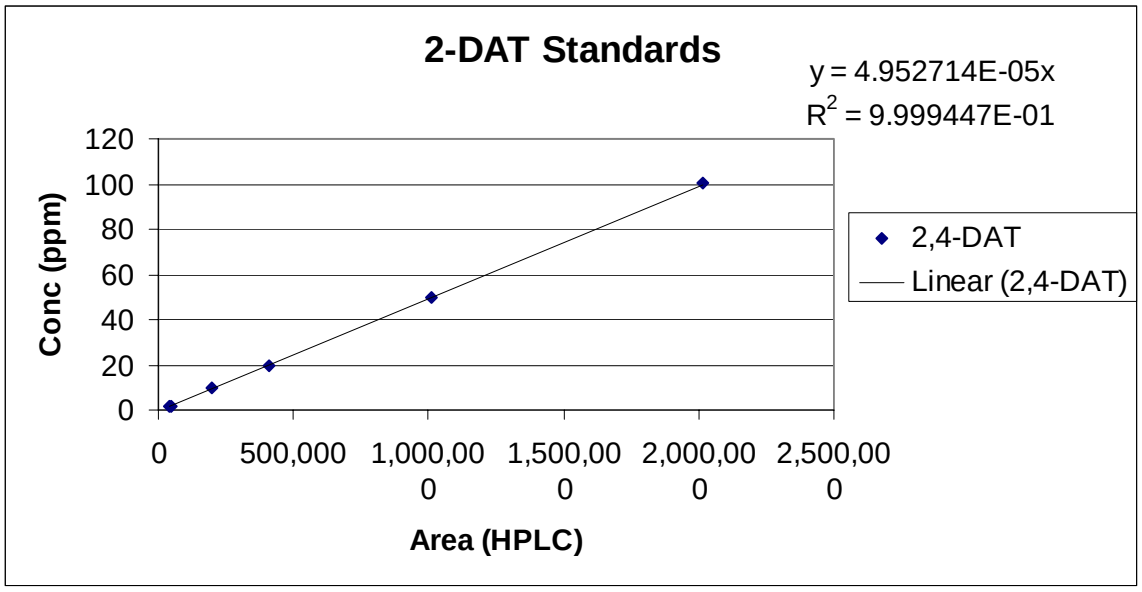


Figure C.4 HPLC Standard Curve with Linear Regression for 2,4-DAT.

2-NT

2-nitrotoluene

Standards run through HPLC, 22 Aug 2003

2-NT 2-nitrotoluene

Time	Concentration (ppm)	Area
7.333	100	2,849,514
7.313	50	1,476,692
7.371	20	584,998
7.351	10	295,034
7.320	2	62,643

Table C.5 HPLC Data for 2-NT Standard

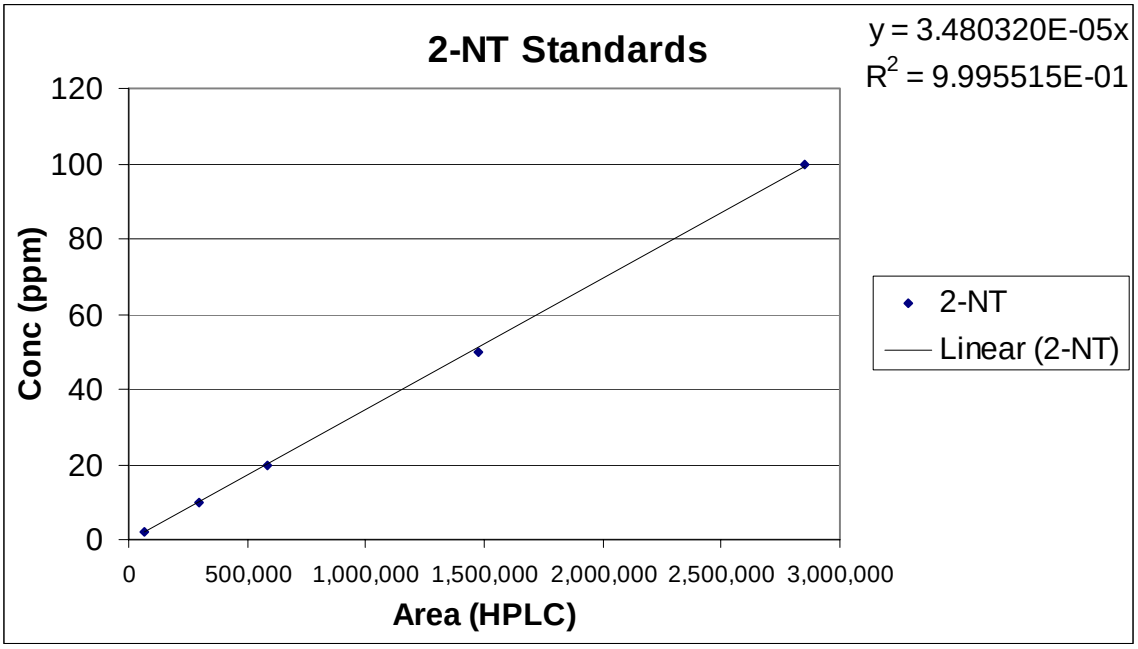


Figure C.5 HPLC Standard Curve with Linear Regression for 2-NT.

2-aT

2-aminotoluene

Standards run through HPLC, 22 Aug 2003
2-aT 2-aminotoluene

Time	Concentration (ppm)	Area
4.280	100	1,045,052
4.281	50	543,037
4.270	20	223,066
4.271	10	99,860
4.288	2	22,115

Table C.6 HPLC Data for 2-aT Standard

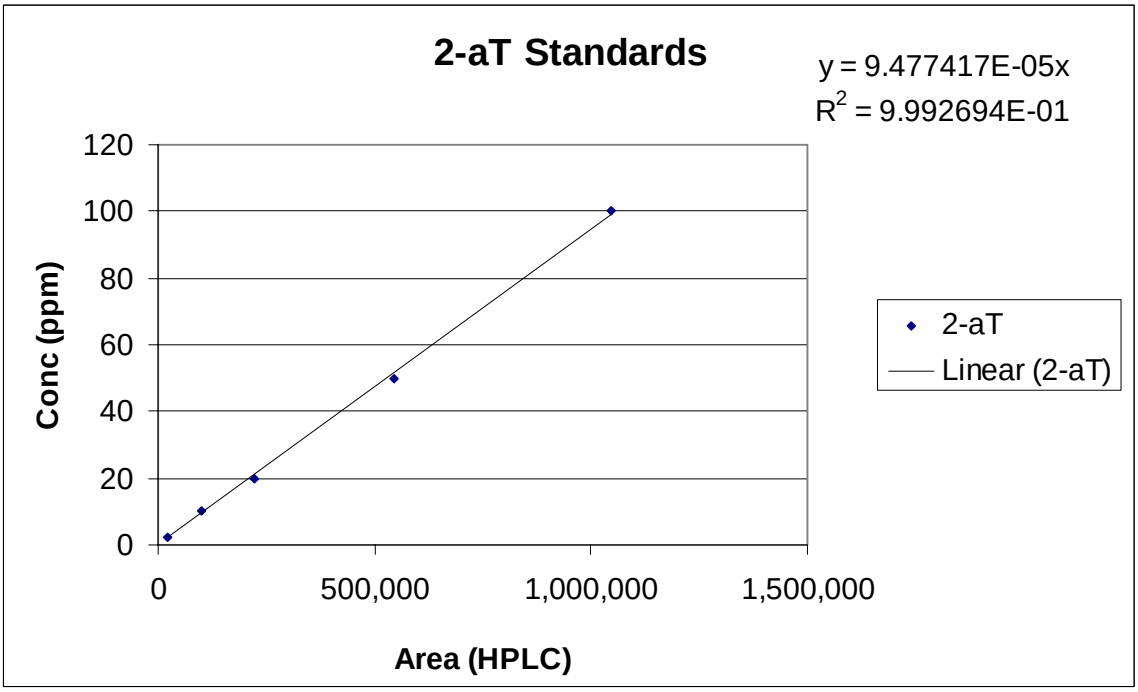


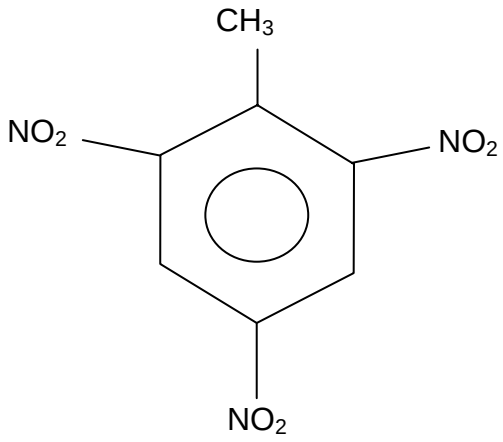
Figure C.6 HPLC Standard Curve with Linear Regression for 2-aT.

APPENDIX D

CONTAMINANT CHEMICAL STRUCTURES

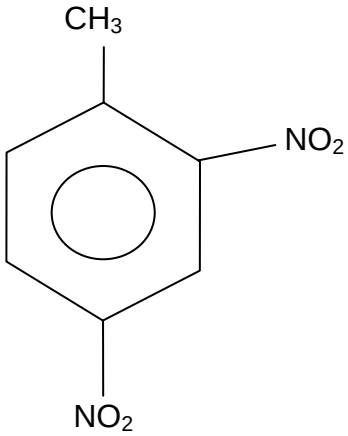
2,4,6-TNT

2,4,6-trinitrotoluene



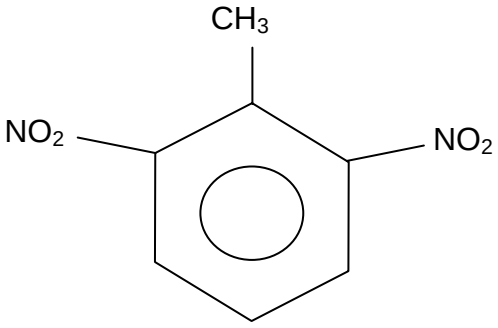
2,4-DNT

2,4-dinitrotoluene



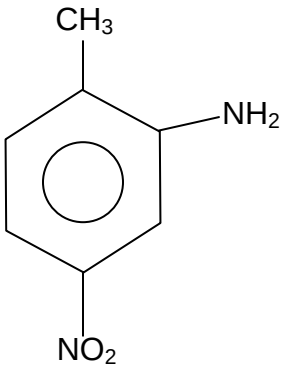
2,6-DNT

2,6-dinitrotoluene



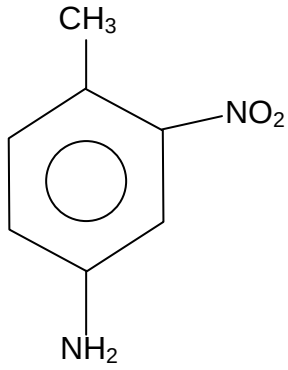
2A4NT

2-amino-4-nitrotoluene
(2-methyl-5-nitroaniline)



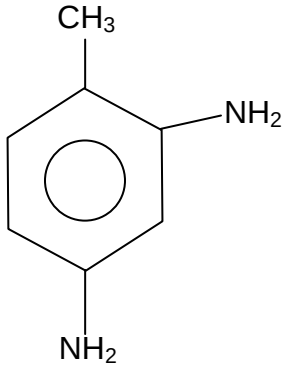
4A2NT

4-amino-2-nitrotoluene
(4-methyl-3-nitroaniline)



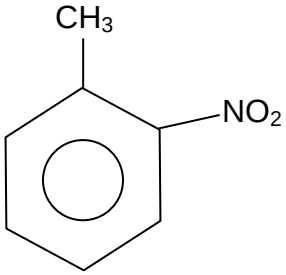
2,4-DAT

2,4-diaminotoluene
(2,4-toluenediamine)



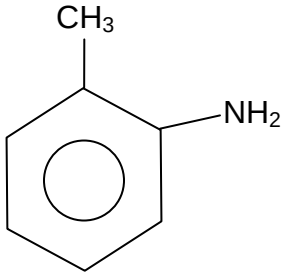
2-NT

2-nitrotoluene
(ortho-nitrotoluene)



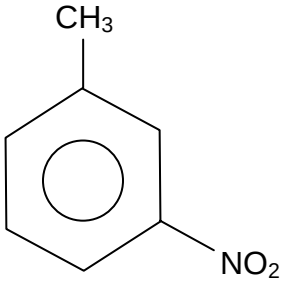
2-aT

2-aminotoluene
(ortho-toluidine)



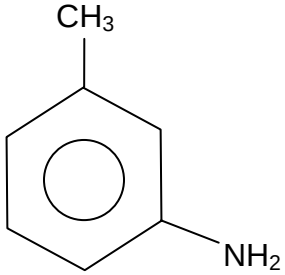
3-NT

3-nitrotoluene
(meta-nitrotoluene)



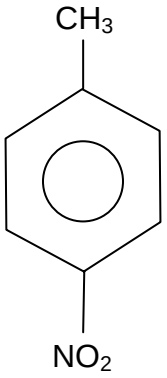
3-aT

2-aminotoluene
(meta-toluidine)



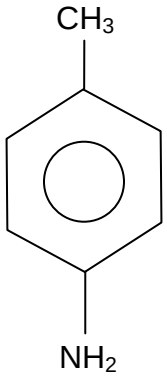
4-NT

4-nitrotoluene
(para-nitrotoluene)



4-aT

4-aminotoluene
(para-toluidine)

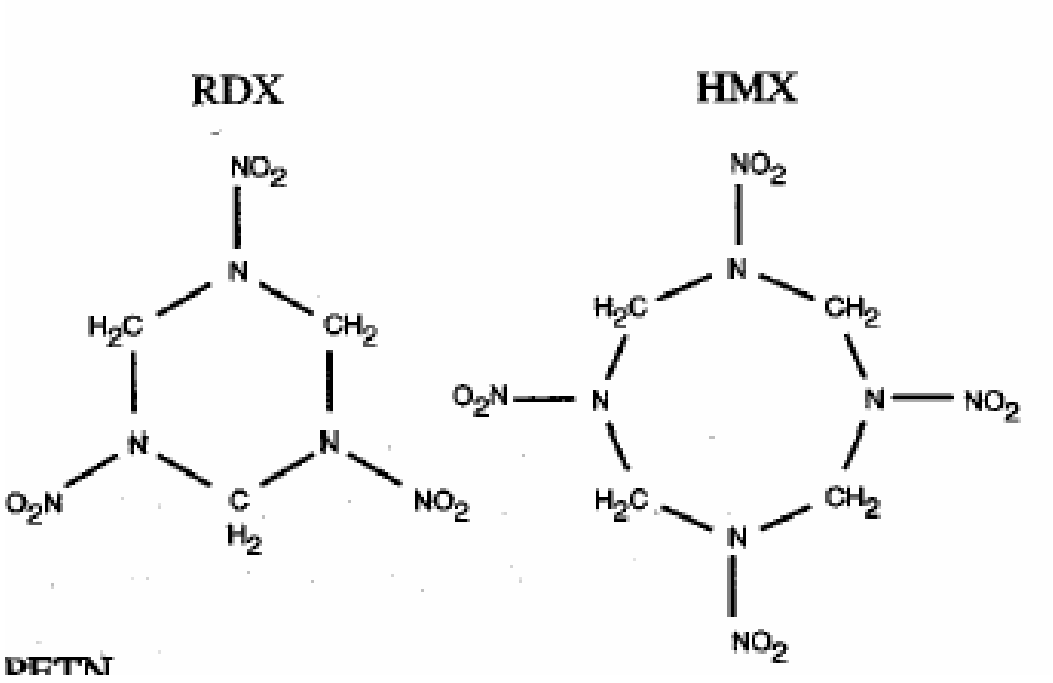


RDX

hexahydro-1,3,5-trinitro-1,3,5-triazine
tetrasocine

HMX

octahydro-1,3,5,7-tetranitro-1,3,5,7-



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14. ABSTRACT
The Department of Defense is responsible for over 2,000 hazardous waste sites containing nitroaromatic compounds (NACs) such as 2,4,6-TNT, 2,4- and 2,6-DNT that resulted from the production and use of munitions throughout the nation and world. NACs are typically persistent in natural environments, though they can be oxidized or reduced under engineered conditions. NACs and their reduction products are toxic chemicals and suspected human carcinogens. Both TNT and 2,4-DNT are listed as priority pollutants by the US EPA. This study investigates the effectiveness of using a palladium (Pd) catalyst in concert with formic acid as an electron donor to reduce NACs. If the reduction reaction is rapid and complete, without producing hazardous daughter products, the process may have application as an *in situ* treatment technology to remediate NAC-contaminated groundwater. In this study, formic acid was added into NAC-contaminated water flowing through a laboratory column filled with Pd catalyst. Experimental results using 2,4-DNT as a model NAC indicate reduction rates are dependent on pH, formic acid concentrations, and NAC concentrations. At high NAC concentrations and high pH, reduction rates slowed.. Higher concentrations of formic acid led to greater extent and rates of 2,4-DNT reduction. The amines that would be expected to be produced from 2,4-DNT reduction were identified in the column effluent, along with several unidentified byproducts. Further research is required to identify and characterize the possible risks these unknown byproducts might pose. Based on experimentally observed reaction rates and removal efficiencies, there is potential that Pd-catalyzed reduction using formic acid as a reductant may have application as an *in situ* remediation technology to manage NAC-contaminated groundwater.

15. SUBJECT TERMS
Nitroaromatic compounds (NACs), 2,4-DNT, palladium, formic acid, catalytic reduction

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